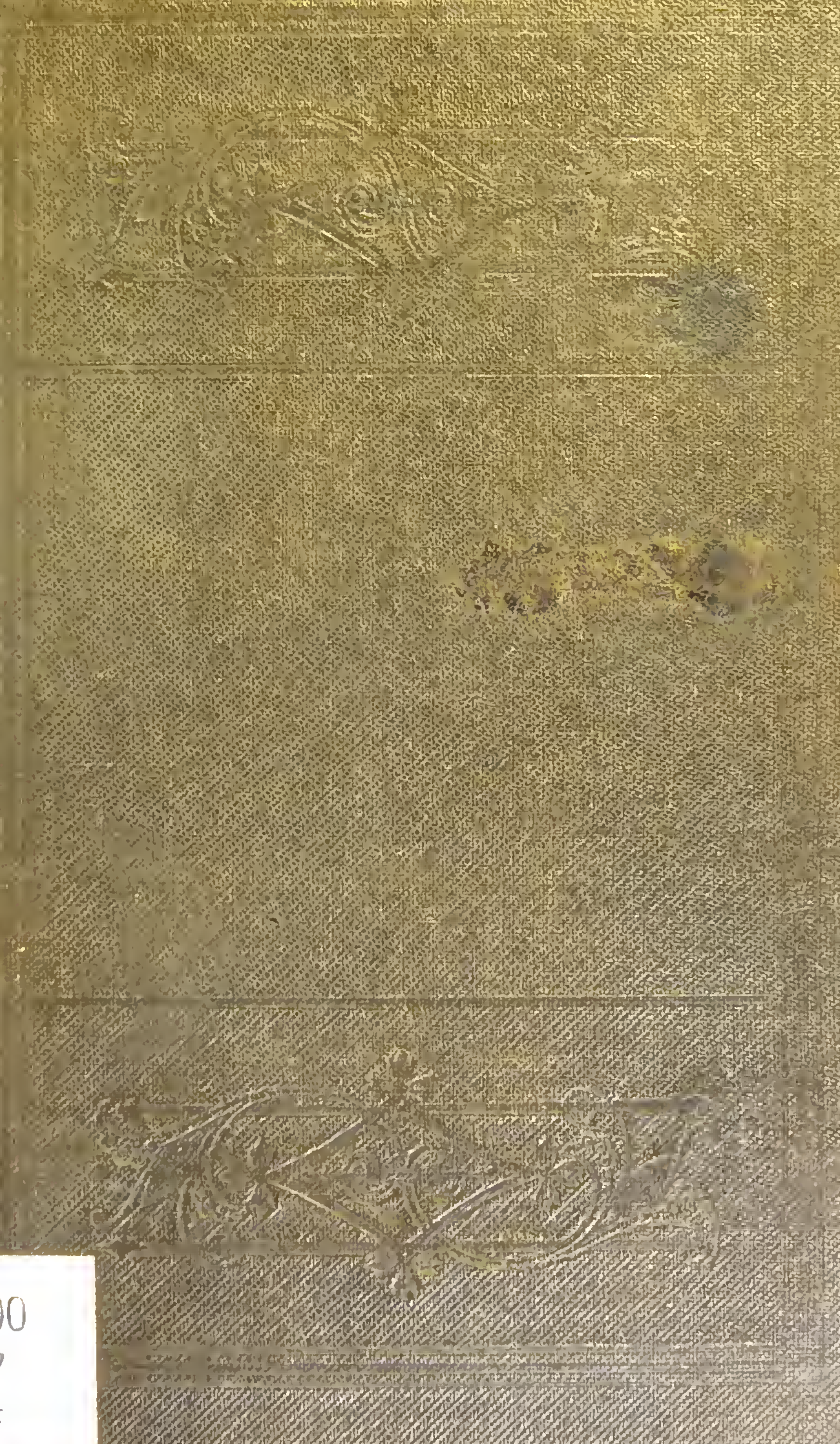

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CHEMISTRY OF CARBON-COMPOUNDS

OR

ORGANIC CHEMISTRY

FOWNES'

MANUAL OF CHEMISTRY

THEORETICAL AND PRACTICAL

VOL. II.

CHEMISTRY OF CARBON-COMPOUNDS
OR
ORGANIC CHEMISTRY

TWELFTH EDITION, REVISED AND ENLARGED

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PREFACE.

THE division of this Manual into two volumes has afforded the means of treating the subject of ORGANIC CHEMISTRY more fully than was possible in the previous Editions.

The arrangement adopted in the present Edition is the same in principle as in the last, organic compounds being classified according to their chemical structure and functions—as Hydrocarbons, Alcohols, Ethers, Acids, Bases, &c., and the compounds in each group arranged in Homologous Series.

Particular attention has been given to the study of Isomerism, especially amongst the Derivatives of Benzene, our knowledge of the isomeric relations of these bodies having lately attained — through the classical researches of Koerner and other distinguished chemists —a high degree of precision and completeness. This part of the subject is here presented in a form in which it has not yet appeared in any English publication, except the "Journal of the Chemical Society."

The portion of the previous Editions relating to Physiological Chemistry—including the description of the Tissues and Fluids of the Animal Body, and the Functions of Nutrition and Respiration—is omitted in the present Edition, this department of Chemistry having now become so extensive as to require treatment in separate works.

HENRY WATTS.

September 1877.

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A

MANUAL OF CHEMISTRY.

VOL. II.

CHEMISTRY OF CARBON-COMPOUNDS

OR

ORGANIC CHEMISTRY.

INTRODUCTION.

THE term "Organic Chemistry" originally denoted the chemistry of compounds formed in the bodies of plants and animals. The peculiar characters of the compounds thus formed, and the failure of the earlier attempts to produce them by artificial means, led to the erroneous idea that their formation was due to a mysterious power, called "vital force," supposed to reside in the living organism, and to govern all the changes and processes taking place within it. In accordance with this idea, the chemistry of organic compounds, including those which were formed by artificial processes from the products of vegetable and animal life, was erected into a special branch of chemical science.

Later researches have, however, shown that a large number of compounds, formerly regarded as producible only under the influence of the so-called vital force, may be formed either by direct combination of their elements, or by chemical transformation of inorganic compounds.

The first step in the formation of organic compounds from their elements was made by Wöhler, who showed, in 1828, that urea, the characteristic constituent of urine, can be produced by molecular transformation of ammonium cyanate. This experiment, viewed in connection with the fact established about twelve years afterwards, that cyanogen (CN) can be formed by direct combination of its elements, is conclusive of the possibility of forming a product of the living organism from inorganic materials. More recently it has been shown that ethine, or acetylene, C_2H_2, can be produced by the direct combination of carbon and hydrogen; that this compound can be made to take up two additional atoms of hydrogen to form ethene, C_2H_4; and that this latter compound can be converted into alcohol, C_2H_6O, a body formerly supposed to be producible only by the fermentation of sugar; and from this a large number of other compounds can be produced by the action of various reagents. The researches of Berthelot, Kolbe, Wurtz, and other distinguished chemists, have led to the discovery of a large number of other cases of the formation of organic compounds, often of great complexity, from substances of purely mineral origin, and ultimately from the elements themselves. The division of compounds into two distinct branches, inorganic and organic—formed according to distinct laws, the former being artificially producible by direct combination of their elements, the latter only under the influence of a supposed vital force—must therefore be abandoned. There is, indeed, but one science of chemistry, of which the study of the compounds called organic forms a part.

Organic chemistry is in fact the chemistry of carbon-compounds, and, in a strictly systematic arrangement, these compounds should be described in connection with the element carbon itself. But the compounds into which carbon enters are so numerous, their constitution and the transformations which they undergo under the influence of heat and of chemical reagents are, in many instances, so complicated, that it is found best, for the purposes of instruction, to defer their consideration till the other elements and their compounds have been studied.

It is important, in this place, to mark the distinction between organic compounds and organised bodies. Organic bodies, such as marsh gas, ethene, benzene, alcohol, sugar, morphine, &c., are definite chemical compounds, many of which, as already observed, may be formed by artificial methods; those which are solid can, for the most part, be crystallised; those which are liquid exhibit constant boiling points. Organised bodies, on the contrary, always consist of mixtures of several definite compounds. They never crystallise, but exhibit a fibrous or cellular structure, and cannot be reduced to the liquid or gaseous state without complete decomposition. Lastly, they are organs, or parts of organs, which are essentially products of vitality, and there is not the slightest prospect of their ever being produced by artificial means.

The study of the composition and chemical relations of organised bodies belongs to a special department of the science called "Physiological Chemistry," which bears the same relation to Organic Chemistry that Chemical Geology bears to Mineralogy.

DECOMPOSITIONS AND TRANSFORMATIONS OF ORGANIC COMPOUNDS.

Organic bodies are, generally speaking, distinguished by the facility with which they decompose under the influence of heat or of chemical reagents; the more complex the body, the more easily does it undergo decomposition or transformation.

1. *Action of Heat.*—Organic bodies of simple constitution and of some permanence, but not capable of subliming unchanged, like many of the organic acids, yield, when exposed to a high but regulated temperature, in a retort, new compounds, perfectly definite and often crystallisable, which partake, to a certain extent, of the properties of the original substance. Carbon dioxide and water are often eliminated under these circumstances. If the heat be suddenly raised to redness, the regularity of the decomposition vanishes, while the products become more uncertain and more numerous; carbon dioxide and watery vapour are succeeded by inflammable gases, as carbon monoxide and hydrocarbons; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is *dry* or *destructive distillation.*

If the organic substance contains nitrogen, and is not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, or substances analogous to it, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

A much greater degree of regularity is observed in the effects of heat on fixed organic matters, when these are previously mixed with an excess of strong alkaline base, as potash or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced, and remains in union with the base, the residual element or elements escaping in some volatile form. Thus benzoic acid distilled with calcium hydrate, at a dull red heat, yields calcium carbonate and benzene; woody fibre and caustic potash, heated to a very moderate temperature, yield free hydrogen, and a brown, somewhat indefinite substance called *ulmic acid;* with a higher degree of heat, oxalic acid appears in the place of the ulmic; and, at the temperature of ignition, carbon dioxide, hydrogen being the other product.

2. *Action of Oxygen.*—Oxygen, either free or in the nascent state, in which latter condition it is most active, may act on organic compounds in four different ways:—

α. By simple addition, as

$$\underset{\text{Aldehyde.}}{C_2H_4O} + O = \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

β. By simply removing hydrogen:

$$\underset{\text{Alcohol.}}{C_2H_6O} + O = H_2O + \underset{\text{Aldehyde.}}{C_2H_4O}$$

γ. By removing hydrogen and taking its place, 2 atoms of hydrogen being replaced by one of oxygen; *e.g.:*

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = H_2O + \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

δ. By removing both carbon and hydrogen. In this manner complex organic bodies containing large numbers of carbon and hydrogen atoms are reduced to others of simpler constitution, and ultimately the carbon and hydrogen are wholly converted into carbon dioxide and water. Nitrogen, chlorine, bromine, and iodine, if present, are at the same time disengaged, for the most part in the free state, and sulphur is oxidised.

Moist organic substances, especially those containing nitrogen, undergo, when exposed to the air, a slow process of oxidation, by which the organic matter is gradually burned and destroyed without sensible elevation of temperature : this process is called *Decay*, or *Eremacausis.* Closely connected with this change are those called *Fermentation* and *Putrefaction*, consisting in a new arrangement of the elements of the compound (often with assimilation of the elements of water), and the consequent formation of new products. The change is called *putrefaction*, when it is accompanied by an offensive odour ; *fermentation*, when no such odour is evolved, and especially if the change results in the formation of useful products ; thus the decomposition of a dead body, or of blood or urine, is putrefaction ; that of grape-juice or malt-wort, which yields alcohol, is fermentation. Putrefaction and fermentation are not processes of oxidation ; nevertheless, the presence of oxygen appears to be indispensable to their commencement ; but the change, when once begun, proceeds without the aid of any other substance external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay ; and if the decay, or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as milk, highly azotised vegetables, and animal flesh intended for food, may be preserved indefinitely, by inclosure in metallic cases from which the air has been *completely* removed and excluded.

Fermentation and putrefaction are always accompanied by the development of certain living organisms of the fungous class ; but whether the growth of these is a cause or a consequence of the chemical change is a point not yet decided. We shall return to this subject in speaking of the fermentation of sugar.

3. *Action of Chlorine, Bromine, and Iodine.*—Chlorine and bromine exert precisely similar actions on organic bodies ; that of chlorine is the more energetic of the two. The reactions consist :

α. In simple addition of chlorine or bromine to the organic molecule ; *e.g.*:

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + Br_2 = \underset{\text{Dibromosuccinic acid.}}{C_4H_4Br_2O_4}$$

β. In removal of hydrogen without substitution :

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 = 2HCl + \underset{\text{Aldehyde.}}{C_2H_4O}$$

γ. In substitution of chlorine or bromine for hydrogen :

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + Cl_2 = HCl + \underset{\text{Chloracetic acid.}}{C_2H_3ClO_2}$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + 3Cl_2 = 3HCl + \underset{\text{Trichloracetic acid.}}{C_2HCl_3O_2}$$

The substitution-products thus formed undergo transformations closely analogous to those of the original compounds, under the influence of similar reagents; but they are always more acid, or less basylous, in proportion to the quantity of chlorine or bromine substituted for hydrogen. Thus aniline, C_6H_7N, which is a strong base, may be converted, by processes to be hereafter described, into the chlorinated compounds, C_6H_6ClN, $C_6H_5Cl_2N$, and $C_6H_4Cl_3N$, the first and second of which are less basic than aniline itself, while the third does not show any tendency to form salts with acids.

δ. In presence of water they remove the hydrogen of that liquid, and set free the oxygen : hence, chlorine-water and bromine-water act as powerful oxidising agents.

Iodine may also act in this manner as an oxidising agent ; and it sometimes attaches itself directly to organic molecules ; but it never acts directly by substitution. Iodine substitution-products may, however, be obtained in some cases by treating organic bodies with chloride of iodine, the chlorine then removing hydrogen, and the iodine taking its place.

4. *Action of Nitric Acid.*—This acid acts very powerfully on organic substances. The action may be of three kinds :

α. Direct combination, as with organic bases ; *e.g.* :

$$\underset{\text{Ethylamine.}}{C_2H_7N} + \underset{\text{Nitric acid.}}{NO_3H} = \underset{\text{Ethylamine nitrate.}}{C_2H_7N.NO_3H}$$

β. Oxidation. This mode of action is most frequently observed with the somewhat diluted acid.

γ. Substitution of nitryl (NO_2) for hydrogen ; *e.g.* :

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{NO_2(OH)} = H_2O + \underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)}$$

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3NO_2(OH)} = 3H_2O + \underset{\text{Trinitrocellulose (gun-cotton).}}{C_6H_7(NO_2)_3O_5}$$

This action takes place most readily with the strongest nitric acid (pure hydrogen nitrate). The products (called nitro-compounds) are always easily combustible, and in many cases highly explosive.

5. *Action of Alkalis.*—The hydroxides of potassium and sodium

act on organic bodies in a great variety of ways, the most important and general of which are the following :—

α. By direct combination :—

$$\begin{array}{ccccc} CO & + & HKO & = & CHKO_2 \\ \text{Carbon monoxide.} & & \text{Potassium hydroxide.} & & \text{Potassium formate.} \end{array}$$

$$\begin{array}{ccccc} C_{10}H_{16}O & + & HKO & = & C_{10}H_{17}KO_2 \\ \text{Camphor.} & & \text{Potassium hydroxide.} & & \text{Potassium campholate.} \end{array}$$

β. By double decomposition with acids, water being eliminated, and a salt produced :

$$\begin{array}{ccccccc} C_2H_4O_2 & + & HKO & = & H_2O & + & C_2H_3KO_2 \\ \text{Acetic acid.} & & & & & & \text{Potassium acetate.} \end{array}$$

γ. Oxidation, with elimination of hydrogen :

$$\begin{array}{ccccccc} C_2H_6O & + & HKO & = & C_2H_3KO_2 & + & 2H_2 \\ \text{Alcohol.} & & & & \text{Potassium acetate.} & & \end{array}$$

δ. From chlorinated compounds they remove a part or the whole of the chlorine :

$$\begin{array}{ccccccccc} C_2H_4Cl_2 & + & HKO & = & C_2H_3Cl & + & KCl & + & H_2O \\ \text{Ethene chloride} & & & & \text{Chlorethene} & & & & \end{array}$$

$$\begin{array}{ccccccccc} C_5H_{11}Cl & + & HKO & = & C_5H_{10} & + & KCl & + & H_2O \\ \text{Amyl chloride.} & & & & \text{Amylene} & & & & \end{array}$$

ε. Amides (i. 361 ; ii. 26) are decomposed by them in such a manner that the whole of the nitrogen is given off as ammonia, and a potassium or sodium salt of the corresponding acid is produced :

$$\begin{array}{ccccccc} NH_2.C_2H_3O & + & HKO & = & NH_3 & + & C_2H_3O.OK \\ \text{Acetamide.} & & & & & & \text{Potassium acetate.} \end{array}$$

Many other azotised organic compounds, when heated with alkaline hydroxides, likewise give up the whole of their hydrogen in the form of ammonia.

6. *Action of Reducing Agents.*—This name is given to bodies whose action is the inverse of that of oxygen, chlorine, bromine, and iodine ; such are nascent hydrogen, obtained by the action of sodium-amalgam on water, or by that of zinc on aqueous acids or alkalis ; also hydrogen sulphide, ammonium sulphide, sulphurous acid, and metals, especially potassium and sodium,—all of which either give up hydrogen, or abstract oxygen, chlorine, &c.

Reducing agents may act in the following ways :—

α. By adding hydrogen to an organic body :

$$\underset{\text{Ethene oxide.}}{C_2H_4O} + HH = \underset{\text{Alcohol.}}{C_2H_6O}$$

β. By removing oxygen, chlorine, bromine, or iodine, without introducing any thing in its place ; thus :

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + HH = H_2O + \underset{\text{Benzoic aldehyde.}}{C_7H_6O}$$

γ. By substituting hydrogen for oxygen, chlorine, &c. This process is called *inverse substitution.* It may take place either in equivalent quantities ; *e.g.* :

$$\underset{\text{Benzoic acid.}}{C_7H_5O.OH} + 2HH = H_2O + \underset{\text{Benzylic alcohol.}}{C_7H_7.OH} ;$$

or it may happen that the quantity of hydrogen introduced is only half that which is equivalent to the oxygen removed. This mode of substitution takes place with nitro-compounds, which are thereby reduced to others containing amidogen (NH_2) in place of nitryl (NO_2) ; thus :

$$\underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + 3H_2 = 2H_2O + \underset{\text{Amidobenzene (aniline).}}{C_6H_5(NH_2)}$$

A large number of organic bases are formed in this manner from nitro-compounds.

7. *Action of Dehydrating Agents.*—Strong sulphuric acid, sulphuric oxide, phosphoric oxide, and zinc chloride, remove oxygen and hydrogen from organic bodies in the form of water, the elements of which are derived, sometimes from a single molecule of the organic body, sometimes from two molecules :

$$\underset{\text{Alcohol.}}{C_2H_6O} - H_2O = \underset{\text{Ethene.}}{C_2H_4}$$

$$\underset{\text{Alcohol.}}{2C_2H_6O} - H_2O = \underset{\text{Ether.}}{C_4H_{10}O}$$

Compounds which, like sugar, starch, and woody fibre, consist of carbon united with hydrogen and oxygen in the proportions to form water, are often reduced by these dehydrating agents to black substances consisting mainly of carbon.

Other reactions of less generality than those above described will be sufficiently illustrated by special cases in the sequel.

THE ELEMENTARY OR ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

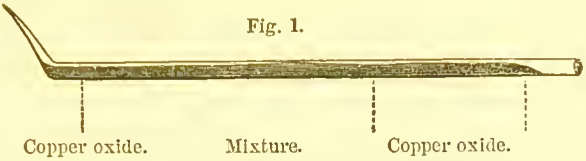
Organic compounds contain, for the most part, only a small number of elements. Many consist only of carbon and hydrogen. A very large number, including most of those which occur ready-formed in the bodies of plants and animals, consist of carbon, hydrogen, and oxygen; others consist of carbon, hydrogen, and nitrogen. Others, again, including most of the proximate principles of the animal organism, consist of four elements, carbon, hydrogen, oxygen, and nitrogen. Some contain sulphur, phosphorus, chlorine, and metallic elements; in fact, artificially prepared carbon compounds may contain any elements whatever. Moreover, even those which contain only a small number of elements often exhibit great complexity of structure, in consequence of the accumulation of a large nnmber of carbon-atoms in the same molecule.

Determination of Carbon and Hydrogen.—The quantities of these elements are determined by heating a known weight of the body to be analysed in contact with some easily reducible metallic oxide, black oxide of copper being the substance generally used. The organic body then undergoes complete combustion at the expense of the oxygen of the copper oxide, the carbon being converted into carbon dioxide, and the hydrogen into water. These prodncts are collected and their weights determined, and from the data thus obtained the quantities of carbon and hydrogen present in the organic substance are calculated. When nothing but carbon and hydrogen, or those bodies together with oxygen, is present, one experiment suffices; the carbon and hydrogen are determined directly, and the oxygen by difference.

The substance to be analysed, if solid, must be carefully freed from moisture. If it will bear the application of a moderate heat, this desiccation is very easily accomplished by a water or steam bath: in other cases, exposure at common temperatures to the absorbent powers of a large surface of oil of vitriol in the vacuum of an air-pump must be substituted.

The copper oxide is best made from the nitrate by complete ignition in an earthen crucible; it is reduced to powder and re-heated just before use, to expel hygroscopic moisture, which it absorbs with avidity, even while warm. The combustion is performed in a tube of hard white Bohemian glass, having a diameter of 0·4 or 0·5 inch, and varying in length from 14 to 18 inches: this kind of glass bears a moderate red heat without becoming soft enough to lose its shape. One end of the tube is drawn out to a point, as shown in fig. 1, and closed; the other is simply heated to fuse and soften the sharp edges of the glass. To prevent absorption of moisture by the copper oxide during the filling of the tube, the oxide, while still hot, is poured into a long-necked flask closed by a cork; it is then left to cool, and afterwards mixed with the organic substance in the combustion tube itself. A small quantity of the cooled oxide is first introduced into the tube, then a portion

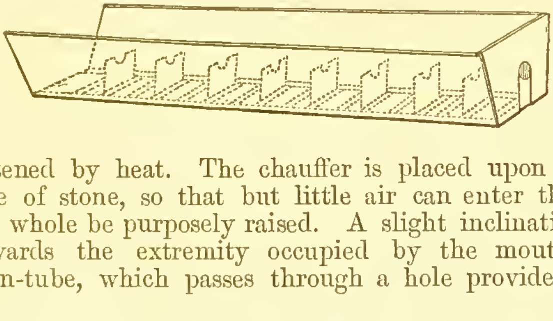
Fig. 1.



of the organic substance is added, and upon this a column of oxide about 3 inches long is poured in the same manner as before. This portion of oxide is mixed with the organic substance by stirring it with a clean iron rod, the extremity of which is bent into two turns of a screw; and when it is thoroughly incorporated, the rest of the substance is introduced, then another column of oxide of the same length as before, and the stirring is repeated. Lastly, the rest of the tube is filled with pure oxide.

The tube is then ready to be placed in the furnace or chauffer: this, when charcoal is the fuel employed, is constructed of thin sheet-iron, and is furnished with a series of supports of equal height, which serve to prevent flexure of the combustion-tube

Fig. 2.



when softened by heat. The chauffer is placed upon flat bricks or a piece of stone, so that but little air can enter the grating, unless the whole be purposely raised. A slight inclination is also given towards the extremity occupied by the mouth of the combustion-tube, which passes through a hole provided for that purpose.

To collect the water produced in the experiment, a small light tube of the form represented in fig. 3, or a U-tube, as in fig. 6, filled with fragments of spongy calcium chloride, is attached by a perforated cork, thoroughly dried, to the open extremity of the combustion-tube. The carbon dioxide is absorbed by a solution of caustic potash, of specific gravity 1·27, which is contained in a small glass apparatus on the principle of a Woulfe's bottle, shown in fig. 4. The connection between the latter and the calcium-chloride tube is completed by a little tube of caoutchouc, secured with silk cord. The whole is shown in fig. 5, as arranged for use.

The tightness of the junctions may be ascertained by slightly rarefying the included air by sucking a few bubbles from the interior through the liquid, using the dry lips, or, better, a little bent tube with a perforated cork ; if the difference of level in the liquid in the two limbs of the potash-apparatus be preserved for several minutes, the joints are perfect. Red-hot charcoal is now placed around the anterior portion of the combustion-tube, containing the pure oxide of copper ; and when this is red-hot, the fire is slowly extended towards the farther extremity by shifting the movable screen represented in the drawing. The experiment must be so conducted, that a uniform stream of carbon dioxide shall enter the potash-apparatus by bubbles which may be easily counted ; when no nitrogen is present, these bubbles are, towards the termination of the experiment, almost completely absorbed by the alkaline liquid, the little residue of air alone escaping. In the case of an azotised body, on the contrary, bubbles of nitrogen gas pass through the potash-solution during the whole process.

Fig. 3.

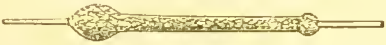


Fig. 4.

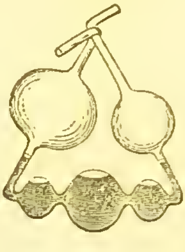
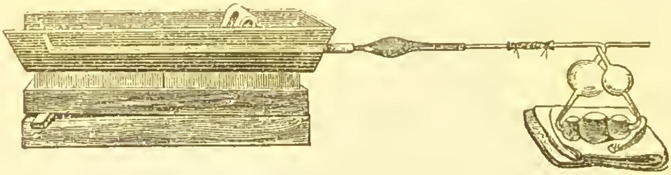


Fig. 5.



Drawing of the whole arrangement.

When the tube has been completely heated from end to end, and no more gas is disengaged, but, on the other hand, absorption begins to be evident, the coals are removed from the farthest extremity of the combustion-tube, and the point of the latter broken off. A little air is drawn through the whole apparatus, by which the remaining carbon dioxide and watery vapour are secured. The parts are, lastly, detached, and the calcium-chloride tube and potash-apparatus re-weighed.

The mode of heating the combustion-tube with red-hot charcoal is the original process, and is still employed where gas is not available. But since the use of coal gas has been universally adopted in laboratories, many contrivances have been suggested, by means of which this convenient fuel may be employed also in organic analysis. An apparatus of this kind* is the one represented in fig. 6, in which the combustion-tube is heated by a series of perforated clay-burners. These clay-burners are fixed on pipes provided with stopcocks, so that the gas may be lighted according to the requirements of the case. The stopcocks being appropriately adjusted, the gas burns on the surface of the burners with a smokeless blue flame, which renders them in a short time incandescent. The construction of this furnace is readily intelligible by a glance at figures 7 and 8, which exhibit the different parts of the apparatus in section, fig. 7 representing a large furnace with five rows, and fig. 8 a smaller furnace with three rows of clay-burners.

Fig. 6.

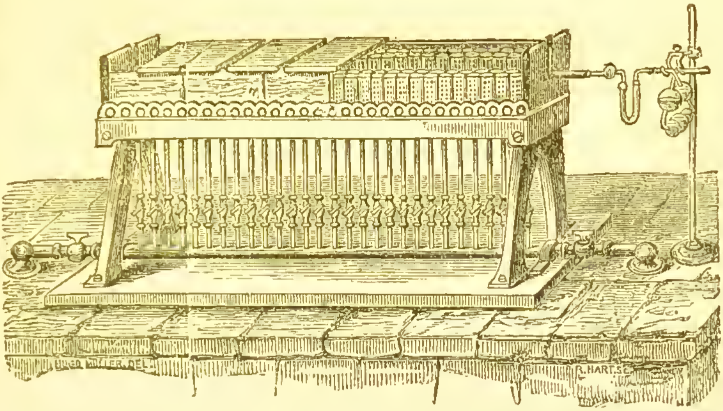


Fig. 7.

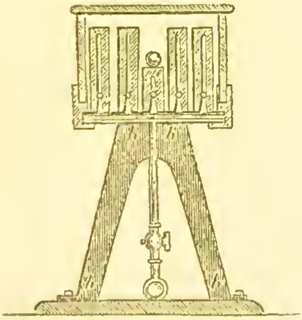
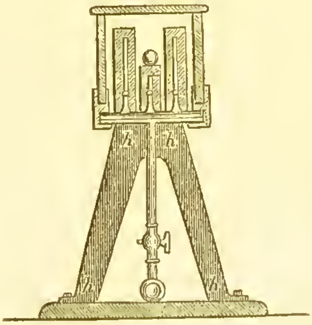


Fig. 8.



Gas-furnaces of simpler construction, in which the combustion-tube is heated by a row of Bunsen burners, are also much used. Such a furnace is that of von Babo, represented in fig. 10.

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* Hofmann, Journal of Chemical Society, vol. xi. p. 30.

The following account of a real experiment will serve to illustrate the calculation of the result obtained in the combustion of crystallised sugar :

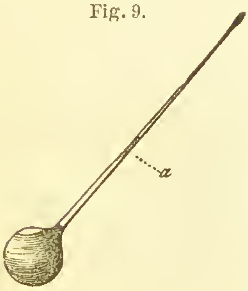
Quantity of sugar employed . . .	4·750 grains.
Potash-apparatus weighed after experiment	781·13
„ „ before experiment	773·82
Carbon dioxide . . .	7·31
Calcium-chloride tube after experiment .	226·05
„ before experiment .	223·30
Water	2·75

7·31 gr. carbon dioxide = 1·994 gr. carbon : and 2·75 gr. water = 0·3056 gr. hydrogen ; or in 100 parts of sugar,*

Carbon	41·98
Hydrogen	6·43
Oxygen, by difference	51·59
	100·00

When the organic substance cannot be mixed with the copper oxide in the manner described, the process must be modified. If, for example, a volatile liquid is to be examined, it is inclosed in a little glass bulb with a narrow stem, which is weighed before and after the introduction of the liquid, the point being hermetically sealed. A little copper oxide is put into the combustion tube, then the bulb, with its stem broken at *a*, a file-scratch having been previously made ; and, lastly, the tube is filled with the cold and dry copper oxide. It is arranged in the furnace, the calcium-chloride tube and potash apparatus adjusted, and then, some 6 or 8 inches of oxide having been heated to redness, the liquid in the bulb is, by the approximation of a hot coal, expelled, and slowly converted into vapour, which, in passing over the hot oxide, is completely burned. The experiment is then terminated in the usual manner. Fatty and waxy substances, and volatile solid bodies, as camphor, are placed in little boats of glass or platinum.

Fig. 9.



Copper oxide which has been used, may be easily restored by moistening with nitric acid, and igniting to redness ; it becomes, in fact, rather improved than otherwise, as, after frequent employ-

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* The theoretical composition of sugar, $C_{12}H_{22}O_{11}$, reckoned to 100 parts, gives—

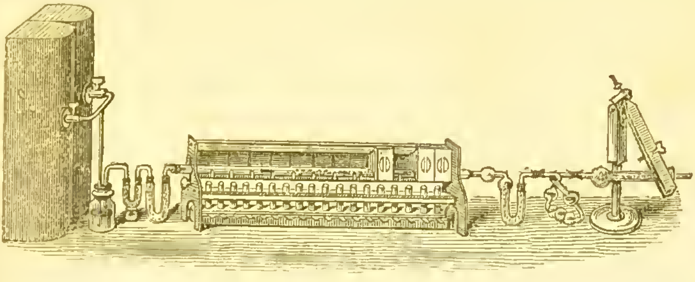
Carbon	42·11
Hydrogen	6·43
Oxygen	51·46
	100·00

ment, its density is increased, and its troublesome hygroscopic powers diminished. For substances which are very difficult of combustion, from the large proportion of carbon they contain, and for compounds into which chlorine enters as a constitutent, fused and powdered lead chromate may be substituted for the copper oxide, as it freely gives up oxygen to combustible matters, and even evolves, when strongly heated, a little of that gas, which thus ensures the perfect combustion of the organic body.

Lead chromate is, however, troublesome to prepare, and always destroys the glass tubes. A more convenient method of insuring the complete combustion of substances which burn with difficulty is to finish the combustion in a stream of oxygen. This may be effected either by placing a small quantity of fused potassium chlorate at the closed end of the combustion-tube, or by connecting the tube with a gas-holder containing oxygen gas. The latter method is to be preferred, as it enables the operator to regulate the stream of gas at his pleasure, whereas the ignition of potassium chlorate is apt to give rise to a rapid evolution of gas, which may force a portion of liquid out of the potash-bulbs and render the analysis worthless.

A form of apparatus for supplying a stream of oxygen is represented in figure 10. The combustion-tube is open at both ends, and the end *a*, farthest from the potash-bulbs and calcium-chloride tube, is connected with two gas-holders, one filled with air, the other with oxygen-gas. The communication is made by means of a T-tube provided with a stop-cock, so that either gas-holder may be connected with the combustion-tube and the other shut off at the same time. The air and oxygen, before entering the combustion-tube, are made to pass through two U-tubes, one containing lumps of pumice soaked in sulphuric acid to dry the gas, the other containing lumps of caustic potash to free it from carbonic acid.

Fig. 10.



The combustion-tube may be heated either with gas or with charcoal (the figure represents a Babo's gas-apparatus), and the mixture may be disposed in the tube in the way above described—or better, in the case of difficultly combustible bodies—the substance may be placed by itself in a small boat of platinum or porcelain. In this case, the combustion-tube is first filled to two-thirds of its length with copper oxide, which need not be previously ignited, the remaining third, nearest to the gas-holder, being left free to receive the boat. It is then laid in the furnace, and connected in the manner just described with the gas-holder containing atmospheric air; the copper oxide is heated to redness; and a stream of dry air is passed through the tube so as to remove every trace of moisture. The tube is then left to cool; the boat containing the substance is introduced, a plug of recently ignited asbestos having been previously introduced to prevent the copper oxide from coming in contact with it; the calcium-chloride tube and potash-bulbs are attached in the usual manner; and the tube is connected with the gas-holder containing oxygen. The copper oxide is now once more heated to redness, and as soon as it is thoroughly ignited, heat is very cautiously applied to the part of the tube containing the boat, a slow stream of oxygen being passed through the apparatus, sufficient to prevent any backward passage of the gases, but not to cause any free oxygen to pass through the solution of potash. If the oxide of copper exhibits a red colour, indicating reduction, the heating of the substance in the boat must be discontinued till the copper is reoxidised. When at length there is nothing left of the organic substance but black charcoal, the heat may be increased and the stream of oxygen accelerated. In this manner the combustion is soon completed, and when the bubbles of gas appear to pass through the potash without absorption, the process is continued in the same manner for a few minutes longer, and the potash bulbs and calcium-chloride tube are then detached, after air has been passed through the apparatus for a little time to displace the oxygen. Lastly, the stream of air is continued for a sufficient time to effect the complete reoxidation of the copper, which is then ready, without further preparation, for another experiment.

After the tube has cooled, the boat is taken out and re-weighed. If any inorganic matter remains in it (as in the case of a salt) the quantity of this is at once ascertained, if the weight of the boat itself is previously known.

As the stream of hot gas is likely to carry vapour of water with it in passing through the potash-bulbs, whence loss of weight would ensue, a second calcium-chloride tube is attached to the potash-bulbs, as shown in the figure, to arrest any water-vapour thus carried over. This tube is weighed, together with the potash-bulbs, before and after the experiment.

The method just described is capable of giving very exact results; it insures the complete combustion of the carbon, and obviates all danger of an excess of hydrogen arising from moisture in the copper oxide. It likewise saves the trouble of igniting this oxide before the experiment and afterwards treating it with nitric acid. But to insure a good result, especial care must be taken not to heat the substance in the boat too suddenly; otherwise combustible gases will be given off faster than they can be burnt, and the analysis will be worthless.

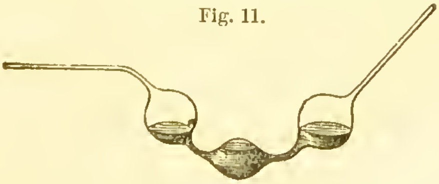
Analysis of Azotised Substances.—The presence of nitrogen in an organic compound is easily ascertained by heating a small portion with solid potassium-hydrate in a test-tube : the nitrogen, if present, is converted into ammonia, which may be recognised by its odour and alkaline reaction.

In determining the carbon and hydrogen in such bodies, by combustion with copper oxide, as above described, a longer tube than usual must be employed, and 4 or 5 inches of its anterior portion filled with copper-turnings rendered perfectly metallic by ignition in hydrogen. This serves to decompose any nitrogen oxides formed in the process of combustion, which, if suffered to pass off undecomposed, would be absorbed by the potash and vitiate the determination of the carbon.

The nitrogen may be estimated either by converting it into ammonia, by igniting the substance with an alkaline hydrate, as above mentioned, or by evolving it in the free state and measuring its volume.

1. By *conversion into Ammonia :* Will and Varrentrapp's method. —An intimate mixture is made of 1 part caustic soda and 2 or 3 parts quicklime, by slaking lime of good quality with the proper proportion of strong caustic soda, drying the mixture in an iron vessel, and then heating it to redness in an earthen crucible. The ignited mass is rubbed to powder in a warm mortar, and carefully preserved from the air. The lime is useful in many ways : it diminishes the tendency of the alkali to deliquesce, facilitates mixture with the organic substance, and prevents fusion and liquefaction. A proper quantity of the substance to be analysed, namely, from 5 to 10 grains, is dried and accurately weighed out : this is mixed in a warm porcelain mortar with enough of the soda-lime to fill two-thirds of an ordinary combustion-tube, the mortar being rinsed with a little more of the alkaline mixture, and, lastly, with a small quantity of powdered glass, which completely removes everything adherent to its surface ; the tube is then filled to within an inch of the open end with the lime-mixture, and arranged in the chauffer in the usual manner. The ammonia is collected in a little apparatus of three bulbs (fig. 11), containing moderately strong hydrochloric acid, attached by a cork to the combustion-tube. Matters being thus adjusted, fire is applied to the tube, commencing with the interior extremity. When it is ignited throughout its whole length, and when no gas issues from the apparatus, the point of the tube is broken, and a little air drawn through the whole. The acid liquid is then emptied into a capsule, the bulbs rinsed into the same,

Fig. 11.



first with a little alcohol, and then repeatedly with distilled water; an excess of pure platinic chloride is added; and the whole evaporated to dryness in a water-bath. The dry mass, when cold, is treated with a mixture of alcohol and ether, which dissolves out the superfluous platinum chloride, but leaves untouched the yellow crystalline ammonium platinochloride. The latter is collected upon a small weighed filter, washed with the same mixture of alcohol and ether, dried at 100°, and weighed; 100 parts correspond to 6·272 parts of nitrogen. Or, the salt with its filter may be very carefully ignited, the filter burned in a platinum crucible, and the nitrogen reckoned from the weight of the spongy metal, 100 parts of that substance being equivalent to 14·18 parts of nitrogen. The former plan is to be preferred in most cases.

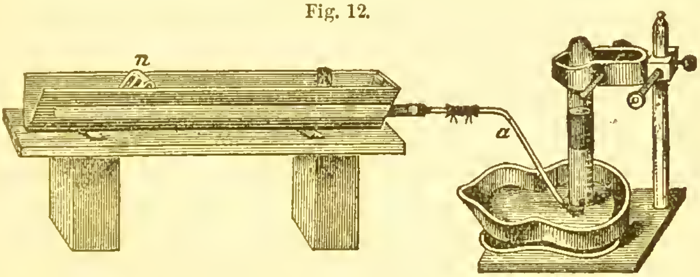
Bodies very rich in nitrogen, as urea, must be mixed with about an equal quantity of pure sugar, to furnish uncondensable gas, and thus diminish the violence of the absorption which otherwise occurs; and the same precaution must be taken, for a different reason, with those which contain little or no hydrogen.

A modification of this process has been suggested by Peligot, which is very convenient if a large number of nitrogen-determinations is to be made. By this plan, the ammonia, instead of being received in hydrochloric acid, is conducted into a known volume ($\frac{1}{2}$ to 1 cubic inch) of a standard solution of sulphuric acid contained in the ordinary nitrogen-bulbs. After the combustion is finished, the acid containing the ammonia is poured out into a beaker, coloured with a drop of tincture of litmus, and then neutralised with a standard solution of soda in water, or of lime in sugar-water, the point of neutralisation becoming perceptible by the sudden appearance of a blue tint. The lime-solution is conveniently poured out from an alkalimeter. The volume of lime-solution necessary to neutralise the same amount of acid that is used for condensing the ammonia, having been ascertained by a preliminary experiment, it is evident that the difference of the quantities used in the two experiments gives the ammonia collected in the acid during the combustion. The amount of nitrogen may thus be calculated. If, for instance, an acid be prepared, containing 20 grains of pure hydrogen sulphate (H_2SO_4) in 1000 grain-measures, then 200 grain-measures of this acid—the quantity introduced into the bulbs—will correspond with 1·38 grains of ammonia, or 1·14 grains of nitrogen. The alkaline solution is so graduated that 1000 grain-measures will exactly neutralise the 200 grain-measures of the standard acid. If we now find that the acid, partly saturated with the ammonia disengaged during the combustion of a nitrogenous substance, requires only 700 grain-measures of the alkaline solution, it is evident that $\frac{200 \times 300}{1000}$ = 60 grain-measures were saturated by the ammonia, and the quantity of nitrogen is obtained by the proportion—$200 : 1{\cdot}14 = 60 : x$, wherefore $x = \frac{1{\cdot}14 \times 60}{200} = 0{\cdot}342$ grain of nitrogen.

2. By *measurement as free Nitrogen.*—When the nitrogen exists in the organic substance in the form of an oxide, as in nitrobenzene, ($C_6H_5(NO_2)$), ethyl nitrite, $C_2H_5(NO)O$, &c., the preceding method cannot be employed, because these nitrogen oxides are not completely converted into ammonia by heating with alkaline hydrates : it fails also in the case of certain organic bases. In such cases the nitrogen must be evolved in the free state by heating the organic body with copper oxide ; and its volume determined by collecting it over mercury in a graduated jar. There are several ways of effecting this : the one most frequently employed is that of Dumas, as simplified by Melsens.

A tube of Bohemian glass, 28 inches long, is securely sealed at one end ; into this enough dry acid sodium carbonate is put to occupy 6 inches. A little pure copper oxide is next introduced, and afterwards the mixture of oxide and organic substance, the weight of the latter, between 4·5 and 9 grains, in a dry state, having been correctly determined. The remainder of the tube, amounting to nearly one-half of its length, is then filled up with pure copper oxide and spongy metal, and a round cork, perforated by a piece of narrow tube, is securely adapted to its mouth. This tube is connected by means of a caoutchouc joint with a bent delivery-tube, *a*, and the combustion-tube is arranged in the furnace. Heat is now applied to the farther end of the tube, so as to decompose a portion of the acid sodium carbonate, the remainder of the carbonate, as well as of the other part of the tube, being protected from the heat by a screen, *n*. The current of carbon dioxide thus produced is intended to expel all the air from the apparatus. In order to ascertain that this object, on which the success of the whole operation depends, is accomplished, the delivery-tube is depressed under the level of a mercurial trough, and the gas, which is evolved, collected in a test-tube filled with concentrated potash-solution. If the gas be perfectly absorbed, or, if after the introduction of a considerable quantity, only a minute bubble be left, the air may be considered as expelled. The next step is to fill a graduated glass jar two-thirds with mercury and one-third with a strong solution of potash, and to invert it over the delivery-tube, as represented in fig. 12.

Fig. 12.



This done, heat is applied to the tube, commencing at the front

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end, and gradually proceeding to the closed extremity, which still contains some undecomposed acid sodium carbonate. This, when the heat at length reaches it, yields up carbon dioxide, which chases forward the nitrogen lingering in the tube. The carbon dioxide generated during the combustion is wholly absorbed by the potash in the jar, and nothing is left but the nitrogen. When the operation is at an end, the jar, with its contents, is transferred to a vessel of water, and the volume of the nitrogen read off. This is properly corrected for temperature, pressure, and aqueous vapour, and its weight determined by calculation. When the operation has been very successful, and all precautions minutely observed, the result still leaves an error in excess, amounting to 0·3 or 0·5 per cent., due to the residual air of the apparatus, or that condensed in the pores of the copper oxide.

A modification of the process, by which this error is considerably diminished, has been devised by Dr. Maxwell Simpson.*

The method just described is applicable to the estimation of nitrogen in the oxides and oxygen-acids of nitrogen, in metallic nitrates and nitrites, and, in fact, to the analysis of all nitrogenous bodies whatever.

Analysis of Chlorinated Compounds.—In the case of a volatile liquid containing chlorine, the combustion with copper oxide must be very carefully conducted, and 2 or 3 inches of the anterior portion of the tube kept cool enough to prevent volatilisation of the copper chloride into the calcium-chloride tube. Lead chromate is much better for the purpose.

The chlorine is determined by placing a small weighed bulb of liquid in a combustion-tube, which is afterwards filled with fragments of pure quicklime. The lime is brought to a red heat, and the vapour of the liquid driven over it, when the chlorine displaces oxygen from the lime, and gives rise to calcium chloride. When cold, the contents of the tube are dissolved in dilute nitric acid, the liquid is filtered, and the chlorine precipitated by silver nitrate.

Bromine and *iodine* are estimated in a similar manner.

Analysis of Organic Compounds containing Sulphur.—When a body of this nature is burned with copper oxide, a small tube containing lead oxide may be interposed between the calcium-chloride tube and the potash apparatus, to retain any sulphurous acid that may be formed. It is better, however, to use lead chromate in such cases. The proportion of sulphur is determined by oxidising a known weight of the substance with strong nitric acid, or by fusion in a silver vessel with ten or twelve times its weight of pure potassium hydrate and half as much nitre. The sulphur is thus converted into sulphuric acid, the quantity of which can be determined by dissolving the fused mass in water, acidulating with nitric acid, and adding a barium salt. *Phosphorus* is, in like manner, oxidised to phosphoric acid, the quantity of which may be determined by precipitation as ammonio-magnesian phosphate.

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* Quarterly Journal of the Chemical Society, vi. 299.

An easier method of estimating sulphur, phosphorus, chlorine, &c., in organic compounds, consists in heating the substance with nitric acid, of specific gravity about 1·2, in a sealed tube. *Sulphur* is thereby, in nearly all cases, completely converted into sulphuric acid, and may be precipitated by chloride of barium; *phosphorus* and *arsenic* are converted into phosphoric and arsenic acids, and may be precipitated as ammonio-magnesium salts; *chlorine* is partly oxidised, partly separated in the free state, but may be completely converted into hydrochloric acid by means of a dilute solution of sulphurous acid or sulphite of sodium, and then precipitated by nitrate of silver; *bromine* and *iodine* are completely separated in the free state, and may be estimated in like manner; lastly, *metals* are converted into oxides or nitrates, and may be estimated by the ordinary methods of mineral analysis.

This method of oxidation by nitric acid in sealed tubes, is likewise applicable to many inorganic compounds, the sulphides of arsenic, for example.

EMPIRICAL AND MOLECULAR FORMULÆ.

A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of the substance to which it refers. A *molecular* formula, on the contrary, expresses the absolute number of atoms of each of its elements supposed to be contained in the molecule, as well as the mere numerical relations existing between them. The empirical formula is at once deduced from the analysis of the substance, reckoned to 100 parts.

The case of sugar, already cited, may be taken as an example. This substance gives by analysis—

Carbon, ...	41·98
Hydrogen, ...	6·43
Oxygen, ...	51·59
	100·00

If each of these quantities be divided by the atomic weight of the corresponding element, the quotients will express the relations existing between the numbers of atoms of the three elements: these are afterwards reduced to their simplest expression. This is the only part of the calculation attended with any difficulty. If the numbers were rigidly correct, it would only be necessary to divide each by the greatest divisor common to the whole; but as they are only approximative, something is of necessity left to the judgment of the experimenter.

In the case of sugar, we have

$$\frac{41·98}{12} = 3·50; \quad \frac{6·43}{1} = 6·43; \quad \frac{51·59}{16} = 3·42,$$

or 350 atoms carbon, 643 atoms hydrogen, and 342 atoms oxygen. Now it is evident, in the first place, that the hydrogen and oxygen are present nearly in the proportions to form water, or twice as many atoms of the former as of the latter. Again, the atoms of carbon and hydrogen are nearly in the proportion of 12 : 22, so that the formula $C_{12}H_{22}O_{11}$ appears likely to be correct. It is now easy to see how far this is admissible, by reckoning it back to 100 parts, comparing the result with the numbers given by the actual analysis, and observing whether the difference falls fairly, in direction and amount, within the limits of error of what may be termed a good experiment, viz., two or three-tenths per cent. *deficiency* in the carbon, and not more than one-tenth or two-tenths per cent. *excess* in the hydrogen :—

Carbon, ...	$12 \times 12 = 144$
Hydrogen, ...	$1 \times 22 = 22$
Oxygen, ...	$16 \times 11 = 176$
	342

$$342 : 144 = 100 : 42·11$$
$$342 : 222 = 100 : 6·43$$
$$342 : 176 = 100 : 51·46$$

To determine the molecular formula, several considerations must be taken into account, namely, the combining or saturating power of the compound, if it is acid or basic ; the number of atoms of any one of its elements (generally hydrogen) which may be replaced by other elements ; the law of even numbers, which requires that the sum of the numbers of atoms of all the perissad elements (hydrogen, nitrogen, chlorine, &c.) contained in the compound shall be divisible by 2 ; and the vapour-density of the compound (if it be volatile without decomposition) which, in normally constituted compounds, is always half the molecular weight (vol. i. p. 253).

The molecular formula may either coincide with the empirical formula, or it may be a multiple of the latter. Thus, the composition of *acetic acid* is expressed by the formula CH_2O, which exhibits the simplest relations of the three elements ; but if we want to express the quantities of these, in atoms, required to make up a molecule of acetic acid, we have to adopt the formula $C_2H_4O_2$: for only one-fourth of the hydrogen in this acid is replaceable by metals to form salts, $C_2H_3KO_2$, for example : and its vapour-density, compared with hydrogen, is nearly 30, which is half the weight of the molecule, $C_2H_4O_2 = 2 . 12 + 4 . 1 + 2 . 16$. Again, the empirical formula of benzene is CH ; but this contains an uneven number of hydrogen-atoms ; moreover, if it expressed the weight of the molecule of benzene, the vapour-density of that compound should be $\frac{12 + 1}{2} = 6·5$, whereas experiment shows that it is six times as great, or equal to 39 : hence the molecular formula of benzene is C_6H_6.

Organic acids and salt-radicles have their molecular weights most frequently determined by an analysis of their lead and silver salts, by burning these latter, with suitable precautions, in a thin porcelain capsule, and noting the weight of the lead oxide or metallic silver left behind. If the lead oxide be mixed with globules of reduced metal, the quantity of the latter must be ascertained by dissolving away the oxide with acetic acid. Or the lead salt may be converted into sulphate, and the silver compound into chloride, and both metals thus estimated. An organic base, on the contrary, has its molecular weight fixed by observation of the quantity of a mineral acid or organic salt-radicle, required to form with it a compound having the characters of neutrality.

The rational and constitutional formulæ of organic compounds will be considered further on.

It is scarcely necessary to observe that the methods just described for determining the empirical and molecular formula of an organic compound from the results of its analysis, together with its physical properties and chemical reactions, are equally applicable to inorganic compounds.

CLASSIFICATION OF ORGANIC COMPOUNDS.—ORGANIC SERIES.

The classification of organic compounds is based upon the quantivalence or atomicity of carbon. This element is a tetrad, being capable of uniting with at most four atoms of hydrogen or other monatomic elements. Methane or marsh gas, CH_4, is therefore a saturated hydrocarbon, not capable of uniting directly with chlorine, bromine, or other monad elements, but only of exchanging a part or the whole of its hydrogen for an equivalent quantity of another monad element. It may, however, as already explained (i. 262), take up any number of dyad elements or radicles, because such a radicle introduced into any group of atoms whatever, neutralises one unit of equivalency, and adds another, leaving therefore the combining capacity or equivalence of the group just the same as before. Accordingly, the hydrocarbon, CH_4, may take up any number of molecules of the bivalent radicle, CH_2, thereby giving rise to the series of saturated hydrocarbons,

$$CH_4, \quad C_2H_6, \quad C_3H_8, \quad C_4H_{10} \ . \ . \ . \ C_nH_{2n+2}.$$

A series of compounds, the terms of which differ from one another by CH_2, is called a homologous series. There are many such series besides that of the hydrocarbons just mentioned; thus methyl chloride, CH_3Cl, gives, by continued addition of CH_2, the series of chlorides,

$$CH_3Cl, \quad C_2H_5Cl, \quad C_3H_7Cl, \quad C_4H_9Cl \ . \ . \ . \ C_nH_{2n+1}Cl;$$

and from methyl alcohol, CH_4O, is derived in like manner the series of homologous alcohols,

$$CH_4O, \quad C_2H_6O, \quad C_3H_8O, \quad C_4H_{10}O \; . \; . \; . \; C_nH_{2n+2}O.$$

The terms of the same homologous series resemble one another in many respects, exhibiting similar transformations under the action of given reagents, and a regular gradation of properties from the lowest to the highest; thus, of the hydrocarbons, C_nH_{2n+2}, the lowest terms CH_4, C_2H_6, and C_3H_8, are gaseous at ordinary temperatures, the highest, containing 20 or more carbon atoms, are solid, while the intermediate compounds are liquids, becoming more and more viscid and less volatile, as they contain a greater number of carbon atoms, and exhibiting a constant rise of about 20° in their boiling points for each addition of CH_2 to the molecule.

The saturated hydrocarbons C_nH_{2n+2}, may, under various circumstances, be deprived of two atoms, or one molecule, of hydrogen, thereby producing a new homologous series,

$$CH_2, \quad C_2H_4, \quad C_3H_6, \quad C_4H_8 \; . \; . \; . \; C_nH_{2n}.$$

These are unsaturated molecules, having two units of equivalency uncombined, and therefore acting as bivalent radicles, capable of taking up 2 atoms of chlorine, bromine, or other univalent radicles, and 1 atom of oxygen or other bivalent radicle.

The first term of this last series cannot give up 2 atoms of hydrogen without being reduced to the atom of carbon; but the remaining terms may each give up 2 atoms of hydrogen, and thus give rise to the series,

$$C_2H_2, \quad C_3H_4, \quad C_4H_6 \; . \; . \; . \; C_nH_{2n-2},$$

each term of which is a quadrivalent radicle.

And, in like manner, by successive abstraction of H_2, a number of homologous series may be formed, whose general terms are

$$C_nH_{2n+2}, \quad C_nH_{2n}, \quad C_nH_{2n-2}, \quad C_nH_{2n-4} \; . \; . \; . \; \&c.$$

The individual series, as far as C_6, are given in the following table, together with the names proposed for them by Dr Hofmann:*

CH_4 Methane	CH_2 Methene					
C_2H_6 Ethane	C_2H_4 Ethene	C_2H_2 Ethine				
C_3H_8 Propane	C_3H_6 Propene	C_3H_4 Propine	C_3H_2 Propone			
C_4H_{10} Quartane	C_4H_8 Quartene	C_4H_6 Quartine	C_4H_4 Quartone	C_4H_2 Quartune		
C_5H_{12} Quintane	C_5H_{10} Quintene	C_5H_8 Quintine	C_5H_6 Quintone	C_5H_4 Quintune	C_5H_2	
C_6H_{14} Sextane	C_6H_{12} Sextene	C_6H_{10} Sextine	C_6H_8 Sextone	C_6H_6 Sextune	C_6H_4	C_6H_2

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* Proceedings of the Royal Society, xv. 57. Names with Greek prefixes are,

Each vertical column of this table forms a homologous series, in which the terms differ by CH_2, and each horizontal line an isologous series, in which the successive terms differ by H_2. The bodies of these last series are designated as the monocarbon, dicarbon group, &c.

The formulæ in the preceding table represent hydrocarbons, all of which are capable of existing in the separate state, and many of which have been actually obtained. They are all derived from saturated molecules, C_nH_{2n+2}, by abstraction of one or more *pairs* of hydrogen-atoms.

But a saturated hydrocarbon, CH_4, for example, may give up 1, 2, 3, or any number of hydrogen atoms in exchange for other elements ; thus, marsh gas, CH_4, subjected to the action of chlorine under various circumstances, yields the substitution-products,

$$CH_3Cl, \quad CH_2Cl_2, \quad CHCl_3, \quad CCl_4,$$

which may be regarded as compounds of chlorine with the radicles,

$$(CH_3)', \quad (CH_2)'', \quad (CH_3)''', \quad C^{iv};$$

and in like manner each hydrocarbon of the series, C_nH_{2n+2}, may yield a series of radicles of the forms,

$$(C_nH_{2n+1})', \quad (C_nH_{2n})'', \quad (C_nH_{2n-1})''', \quad C_nH_{2n-2})^{iv}, \text{ \&c.},$$

each of which has an equivalent value, or combining power, corresponding with the number of hydrogen-atoms abstracted from the original hydrocarbon. Those of even equivalence contain even numbers of hydrogen-atoms, and are identical in composition with those in the table on page 22 ; but those of uneven equivalence contain odd numbers of hydrogen atoms, and are incapable of existing in the separate state, except, perhaps, as double molecules (vol. i. p. 262).

These hydrocarbon radicles of uneven equivalence are designated by names ending in *yl*, those of the univalent radicles being formed from methane, ethane, &c., by changing the termination *ane* into *yl;* those of the trivalent radicles by changing the final *e* in the names of the bivalent radicles, methene, &c., into *yl;* and similarly for the rest. The names of the whole series will therefore be as follows :

CH_4 Methane	$(CH_3)'$ Methyl	$(CH_2)''$ Methene	$(CH)'''$ Methenyl				
C_2H_6 Ethane	$(C_2H_5)'$ Ethyl	$(C_2H_4)''$ Ethene	$(C_2H_3)'''$ Ethenyl	$(C_2H_2)^{iv}$ Ethine	$(CH_2)^{v}$ Ethinyl		
C_3H_8 Propane	$(C_3H_7)'$ Propyl	$(C_3H_6)''$ Propene &c.	$(C_3H_5)'''$ Propenyl	$(C_3H_4)^{iv}$ Propine &c.	$(C_3H_3)^{v}$ Propinyl	$(C_3H_2)^{vi}$ Propone &c.	$(C_3H)^{vii}$ Proponyl

From these hydrocarbon-radicles, called alcohol-radicles, because

however, more generally used; *e.g.*, pentane, hexane, and heptane, rather than quintane, sextane, and septane.

they enter into the composition of alcohols, others of the same degree of equivalence may be derived by partial or total replacement of the hydrogen by other elements, or compound radicles. Thus from propyl, C_3H_7, may be derived the following univalent radicles :

C_3H_6Cl	$C_3H_3Cl_4$	C_3H_5O	$C_3H_2Cl_3O$	$C_3H_6(CN)'$
Chloropropyl.	Tetrachloropropyl.	Oxypropyl.	Trichloroxypropyl.	Cyanopropyl.

$C_3H_6(NO_2)$	$C_3H_4(NH_2)O$	$C_3H_6(CH_3)$	$C_3H_5(C_2H_5)_2$
Nitropropyl.	Amidoxypropyl.	Methyl-propyl.	Diethyl-propyl.

From the radicles above mentioned, all well-defined organic compounds may be supposed to be formed by combination and substitution, each radicle entering into combination just like an elementary body of the same degree of quantivalence.

Organic compounds may thus be arranged in the following classes :—

1. Hydrocarbons containing even numbers of hydrogen atoms.—These are the compounds tabulated on page 22 ; they are sometimes regarded as hydrides of radicles containing uneven numbers of hydrogen atoms, *e.g.*,

Methane, $CH_4 = CH_3.H$ Methyl hydride.

2. Haloïd Ethers.—Compounds of hydrocarbons with halogen elements, *e.g.*,

CH_3Cl	$C_2H_4Br_2$	$C_3H_5I_3$
Methyl chloride.	Ethene bromide.	Propenyl iodide.

3. Compounds of hydrocarbons with nitryl, NO_2 (the radicle of nitric acid, $NO_2.OH$), *e.g.*,

$CH_3.NO_2$	$C_2H_4.(NO_2)_2$
Nitro-methane.	Dinitro-methene.

4. Amines and Nitrils.—Compounds of alcohol-radicles with amidogen (NH_2), imidogen $(NH)''$, and nitrogen (N''') : *e.g.*,

$C_2H_5.NH_2$	$(C_2H_5)_2.NH$	$(C_2H_5)_3N$
Ethylamine.	Diethylamine.	Triethylamine.
$C_2H_4.(NH_2)_2$	$(C_2H_4)_2(NH)_2$	$(C_2H_4)_3.N_2$
Ethene-diamine.	Diethene-diamine.	Triethene-diamine.

These bodies are mostly of basic character, and capable of forming salts with acids, like ammonia, H_3N, from which they may, in fact, be derived by substitution of alcohol-radicles for part or the whole of the hydrogen. Those in which the hydrogen is wholly thus replaced are called nitrils ; and among these special mention must be made of a group consisting of nitrogen combined with a trivalent hydrocarbon-radicle, such as—

$(CH)N$	$(C_2H_3)N$	$(C_3H_5)N$
Methenyl nitril.	Ethenyl nitril.	Propenyl nitril.

These nitrils have no basic properties, but are all neutral, except the first, which is a monobasic acid, capable of exchanging its hydrogen for metals, and in this character may be regarded as a compound of hydrogen with the univalent radicle cyanogen $-C \equiv N$; it is accordingly named hydrogen cyanide, or hydrocyanic acid, and the other nitrils homologous with it are the ethers of this acid; thus:

Methenyl nitril, $(CH)N = CN.H$, Hydrogen cyanide,
Ethenyl nitril, $(C_2H_3)N = CN.CH_3$, Methyl cyanide,
Propenyl nitril, $(C_3H_5)N = CN.C_2H_5$, Ethyl cyanide.

By the combination of amines with the chlorides, hydroxides, &c., of alcohol-radicles, compounds are formed containing pentad nitrogen, and having the composition of ammonium salts, in which the hydrogen is more or less replaced by alcohol radicles; thus:

$N(C_2H_5)H_3Cl$, Ethylammonium chloride,
$N(C_2H_5)_2H_2Cl$, Diethylammonium chloride,
$N(C_2H_5)_3HCl$, Triethylammonium chloride,
$N(C_2H_5)_4Cl$, Tetrethylammonium chloride,
$N(C_2H_5)_4OH$, Tetrethylammonium hydroxide.

This last compound and its analogues, containing methyl, amyl, &c., are powerful alkalis, obtainable, by evaporation of their aqueous solution, as white deliquescent crystalline masses resembling caustic potash.

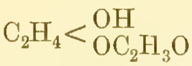
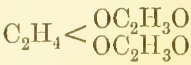
Analogous to the amines are the phosphines, arsines, and stibines,—*e.g.*,

$(C_2H_5)_2.PH$	$(C_2H_5)_3As$	$(C_2H_5)_3Sb$
Diethyl-phosphine.	Triethyl-arsine.	Triethyl-stibine.

5. Alcohols.—Compounds of hydrocarbons with hydroxyl: *e.g.*,

$C_2H_5.OH$	$C_2H_4.(OH)_2$	$C_3H_5.(OH)_3$
Ethyl-alcohol.	Ethene alcohol (Glycol).	Propenyl alcohol (Glycerin).

6. The replacement of the hydroxylic hydrogen in an alcohol by hydrocarbon-radicles (alcohol-radicles), or oxygenated hydrocarbon radicles (acid radicles), gives rise respectively to oxygen-ethers and compound ethers, *e.g.*,

$C_2H_5.O.C_2H_5$	$C_2H_5.O.CH_3$	C_2H_4O
Ethyl oxide.	Ethyl-methyl oxide.	Ethene oxide.
$C_2H_5.O.C_2H_3O$	 $C_2H_4 < \begin{matrix} OH \\ OC_2H_3O \end{matrix}$	 $C_2H_4 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix}$
Ethyl acetate.	Ethene mono-acetate.	Ethene di-acetate.

7. Sulphur and Selenium Alcohols and Ethers.—Compounds analogous to the oxygen alcohols and ethers—the oxygen

being replaced by sulphur or selenium. The sulphur and selenium alcohols are called mercaptans.

8. Compounds of hydrocarbon radicles with various elements, metallic and non-metallic: *e.g.*,

NaC_2H_5 Sodium ethide.
$Zn(C_2H_5)_2$ Zinc ethide.
$Sn(CH_3)_4$ Stannic methide.
$B(C_2H_5)_3$ Triethylic boride.
$Si(C_2H_5)_4$ Tetrethylic silicide.

Those containing metals are called Organo-metallic Compounds.

9. Aldehydes.—Compounds intermediate between alcohols and acids. Thus:

C_2H_6O Ethyl alcohol.
C_2H_4O Acetic aldehyde.
$C_2H_4O_2$ Acetic acid.

10. Ketones.—Bodies derived from aldehydes by the replacement of 1 atom of hydrogen by an alcohol-radicle; *e.g.*,

$$\text{Acetone, } C_3H_6O = C_2H_3(CH_3)O.$$

Organic Acids.—Compounds of oxygenated radicles with hydroxyl; *e.g.*,

$C_2H_3O.HO$ Acetic acid.
$(C_4H_4O_2).(HO)_2$ Succinic acid.
$(C_6H_5O_4).(HO)_3$ Citric acid.

The hydrogen in the radicles of these acids may be more or less replaced by chlorine, bromine, nitryl, amidogen, &c.: thus from benzoic acid, $C_7H_5O.OH$, are derived:

$C_7H_4ClO.OH$ Chlorobenzoic acid.
$C_7H_4(NO_2)O.OH$ Nitrobenzoic acid.
$C_7H_3(NH_2)_2O.OH$ Diamidobenzoic acid.

11. Acid Halides, also called Chlor-anhydrides, Brom-anhydrides, &c.—Compounds of oxygenated radicles (acid radicles) with halogen-elements, and derived from the acids by substitution of those elements for the hydroxyl; *e.g.*,

$C_2H_3O.Cl$ Acetyl chloride.
$C_2H_4O_2.Cl_2$ Succinyl chloride.
$C_6H_5O_4.Cl_3$ Citryl chloride.

12. Acid Oxides, sometimes called *Anhydrous Acids* or *Anhydrides*; *e.g.*,

$(C_2H_3O)_2O$ Acetic oxide.
$C_4H_4O_2.O$ Succinic acid.
$\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O$ Aceti-benzoic oxide.

13. Amides.—Compounds analogous to the amines, but containing

acid-radicles instead of alcohol-radicles: those which contain bivalent radicles combined with imidogen, NH, are called imides; *e g.*,

Acetamide, $C_2H_2O.NH_2$
Diacetamide, $(C_2H_3O)_2.NH$
Succinimide, $C_4H_4O_2.NH$
Succinamide, $C_4H_4O_2(NH_2)_2$
Trisuccinamide, $(C_4H_4O_2)_3N_2$
Citramide, $(C_6H_5O_4)N$

Each of the classes of carbon-compounds above enumerated may be divided into homologous and isologous series, though in most cases these series are far from being complete.

Further, organic compounds may be divided in two great groups, called the Fatty and Aromatic groups, each including hydrocarbons, alcohols, acids, bases, &c., those of the first group being derived from methane, CH_4, and those of the second from benzene, C_6H_6. The corresponding compounds in these two groups are distinguished from one another by well-marked characters, supposed to depend upon the arrangement of the carbon-atoms in their molecules.

The preceding classes, most of which have their analogues amongst inorganic compounds, include nearly all artificially prepared organic bodies, and the majority of those produced in the living organism. There are still, however, many compounds formed in the bodies of plants and animals, the chemical relations of which are not yet sufficiently well made out to enable us to classify them with certainty. Such is the case with many vegetable oils and resins, with most of the alkaloïds or basic nitrogenised compounds found in plants, such as morphine, quinine, strychnine, &c., and several definite compounds formed in the animal organism, as albumin, fibrin, casein, and gelatin.

Rational Formulæ of Organic Compounds.—It must be distinctly understood that the formulæ above given are not the only ones by which the constitution of the several classes of organic compounds may be represented. Rational formulæ are intended to represent the mode of formation and decomposition of compounds, and the relation which allied compounds bear to one another: hence, if a compound can, under varying circumstances, split up into different atomic groups or radicles, or if it can be formed in various ways by the combination of such radicles, different rational formulæ must be assigned to it. This point has been already noticed in connection with the constitution of metallic salts, and illustrated especially in the case of the sulphates (i. 321); but organic compounds, which for the most part contain larger numbers of atoms, and are therefore capable of division into a greater number of groups, afford much more abundant illustration of the same principle. Take, for example, acetic acid, the molecular formula of which is $C_2H_4O_2$. This may be resolved into the following rational formulæ:

1. $C_2H_3O_2.H$.—This formula, analogous to that of hydrochloric acid, $Cl.H$, indicates that a molecule of acetic acid can give up one atom of hydrogen in exchange for a univalent metal or alcohol-

radicle, forming, for example, sodium acetate, $C_2H_3O_2.Na$, ethyl acetate, $C_2H_3O.C_2H_5$, &c.; that two molecules of the acid may give up two hydrogen-atoms in exchange for a bivalent metal or alcohol-radicle, forming barium acetate, $(C_2H_3O_2)_2Ba$, ethene acetate, $(C_2H_3O_2)_2.(C_2H_4)$, &c.; in other words, that acetic acid is a monobasic acid (i. 322).

2. $C_2H_3O.HO$.—This formula, analogous to that of water, $H.HO$, indicates such reactions as the formation of acetic acid from acetic chloride by the action of water:

$$C_2H_3O.Cl + H.HO = HCl + C_2H_3O.HO.$$

3. $C_2H_3O.H.O$.—This formula, also comparable with that of water, $H.H.O$, indicates the conversion of acetic acid into acetic chloride, by the action of phosphorus pentachloride:

$$C_2H_3O.H.O + PCl_3.Cl_2 = C_2H_3O.Cl + HCl + PCl_3O;$$

also the formation of thiacetic acid, $C_2H_3O.H.S$, by the action of phosphorus pentasulphide on acetic acid:

$$5(C_2H_3O.H.O) + P_2S_5 = 5(C_2H_3O.H.S) + P_2O_5.$$

4. $(C_2H_3)'''.HO.O$.—This represents the formation of acetic acid from ethenyl nitril, $(C_2H_3)'''N$, by heating with caustic alkalis:

$$\underset{\text{Ethenyl nitril.}}{(C_2H_3)N} + \underset{\text{Water.}}{\left.\begin{matrix}HH.O\\H.HO\end{matrix}\right\}} = NH_3 + (C_2H_3).O.HO.$$

5. $(CO.CH_3).HO$.—This formula, in which the radicle acetyl, C_2H_3O, is resolved into carbonyl, $(CO)''$, and methyl, represents:

α. The decomposition of acetic acid by electrolysis, in which hydrogen is evolved at the positive pole, while carbon dioxide and ethane, C_2H_6, appear at the negative:

$$2(CO.CH_3.HO) = H_2 + C_2H_6 + 2CO_2.$$

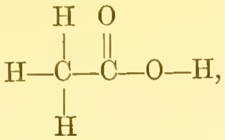
β. The production of methane (marsh gas) by heating potassium acetate with excess of potassium hydroxide (i. 172).

$$\underset{\text{Potassium acetate.}}{CO.CH_3.KO} + \underset{\text{Potassium hydroxide.}}{HKO} = \underset{\text{Methane.}}{CH_4} + \underset{\text{Potassium carbonate.}}{(CO)''.(KO)_2}.$$

γ. The production of acetone and barium carbonate by the dry distillation of barium acetate:

$$\underset{\text{Barium acetate.}}{(CO.CH_3)_2.BaO_2} = \underset{\text{Acetone.}}{(CO)(CH_3)_2} + \underset{\text{Barium carbonate.}}{(CO).BaO_2}.$$

Now, on comparing these several rational formulæ, it will be seen that they are all included under the constitutional formula,



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{O} & & \\ & & | & & \| & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O}-\mathrm{H}, \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{array}$$

in which the molecule is resolved into its component atoms, and these atoms are grouped, as far as possible, according to their different equivalences, or combining capacities. These constitutional formulæ are the nearest approach to the representation of the true constitution of a compound that our knowledge of its reactions enables us to give ; but the student cannot too carefully bear in mind that they are not intended to represent the actual arrangement of the atoms in space, but only, as it were, their relative mode of combination, showing which atoms are combined together directly, and which only indirectly, that is, through the medium of others. Thus, in the formula of acetic acid, it is seen that three of the hydrogen-atoms are united directly with the carbon, while the fourth is united to it only through the medium of oxygen ; that one of the two oxygen-atoms is combined with carbon alone, the other both with carbon and with hydrogen ; and that one of the carbon atoms is combined with the other carbon atom and with hydrogen ; the second with carbon and with oxygen. Abundant illustration of these principles will be afforded by the special descriptions of organic compounds in the following pages.

Isomerism.—Two compounds are said to be isomeric, when they have the same empirical formula or percentage composition, but exhibit different properties. A few examples of isomerism are met with amongst inorganic compounds ; but they are much more numerous amongst organic or carbon compounds.

Isomeric bodies may be divided into two principal groups, namely:

A.—Those which have the same molecular weight ; and these are subdivided into :

α. **Isomeric bodies**, strictly so called, namely, those which exhibit analogous decompositions and transformations when heated, or subjected to the action of the same reagents, and differ only in physical properties. Such is the case with the volatile oils of turpentine, lemons, juniper, &c., all of which have the composition $C_{10}H_{16}$, resemble each other closely in their chemical reactions, and are distinguished chiefly by their odour and their action on polarised light.

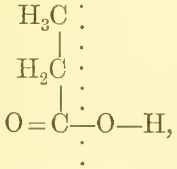
β. **Metameric bodies**, which, with the same percentage composition and molecular weight, exhibit dissimilar transformations under similar circumstances. Thus the molecular formula, $C_3H_6O_2$, represents three different bodies, all exhibiting different modes of decomposition under the influence of caustic alkalis, viz., (1.) Propionic acid, $C_3H_5O.OH$, which is converted by caustic potash, at ordinary temperatures, into potassium propionate, $C_3H_5O.OK$.

(2.) Methyl acetate, $C_2H_3O.OCH_3$, a neutral liquid not acted upon by potash at common temperatures, but yielding, when heated with it, potassium acetate and methyl alcohol :

$$C_2H_3O.OCH_3 + KOH = C_2H_3O.OK + CH_3.OH.$$

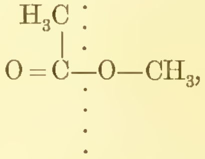
(3) Ethyl formate, $CHO.OC_2H_5$, converted in like manner, by heating with potash, into potassium formate, $CHO.OK$, and ethyl alcohol, $C_2H_5.OH$.

These three compounds may be represented by the following constitutional formulæ, the dotted lines marking the division into radicles indicated by the rational formulæ above given :



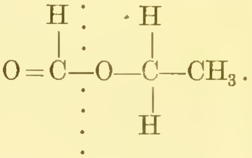
$$\begin{array}{l} H_3C \\ \ \ | \\ H_2C \\ \ \ | \\ O=C-O-H, \end{array}$$

Propionic acid.



$$\begin{array}{l} \quad\ H_3C \\ \qquad | \\ O=C-O-CH_3, \end{array}$$

Methyl acetate.



$$\begin{array}{l} \qquad H \qquad\quad H \\ \qquad | \qquad\quad\ | \\ O=C-O-C-CH_3. \\ \qquad\qquad\quad\ | \\ \qquad\qquad\quad H \end{array}$$

Ethyl formate.

Another kind of metamerism is exhibited by the normal and iso-alcohols and their derivatives, the structure of which will be explained hereafter.

B.—Compounds which have the same percentage composition, but differ in molecular weight ; such bodies are called polymeric. The most striking example of polymerism is exhibited by the hydrocarbons, C_nH_{2n}, all of which are multiples of the lowest, namely, methene, CH_2. Another example is afforded by certain natural volatile oils, which are polymeric with oil of turpentine, $C_{10}H_{16}$, and have the formulæ, $C_{20}H_{32}$, $C_{30}H_{48}$, &c. All polymeric compounds exhibit regular gradations of boiling point, vapour density, and other physical characters, from the lowest to the highest. Some are chemically isomeric, exhibiting analogous transformations under similar circumstances, while others are metameric, exhibiting dissimilar reactions under given circumstances.

PHYSICAL PROPERTIES OF CARBON-COMPOUNDS.

1. **Density and Specific Volume.**—It has been already pointed out (i. 253) that—with a few apparent exceptions depending on decomposition or dissociation at high temperatures—the densities of all compounds in the gaseous state are proportional to their molecular weights ; further that, taking hydrogen as the unit, both of density and of atomic weight, the density of any compound gas or vapour is equal to half its molecular weight ;—and consequently that the specific volume of any compound gas or vapour—that is to say, the quotient of its molecular weight by its density—is equal to 2

In the liquid and solid states the relations between density and molecular weight are less simple ; nevertheless some very remarkable laws have been made out, depending, in the case of solid bodies, chiefly on isomorphism (i. 254).

In the case of carbon compounds, it is principally with reference to the liquid state that general relations between density, molecular weight, and atomic constitution have been discovered.

The specific volumes of liquids are comparable only at those temperatures for which their vapour-tensions are equal, as at the boiling points. If the molecular weights are compared with the densities at equal temperatures, no regular relations can be perceived ; but when the same comparison is made at the boiling points of the respective liquids, several remarkable laws become apparent. The density of a liquid at its boiling point cannot be ascertained by direct experiment, but when the density at any one point, say at 15·5° C., has been determined, and the rate of expansion is also known, the density at the boiling point may be calculated.

The most important of these relations are the following :—

1. In homologous series a difference of CH_2 in the composition answers to a difference of 22 in the specific volume ; thus :

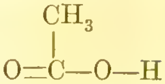
		Molecular Weight.	Specific Volume.	Difference.
Formic acid,	$C\,H_2O_2$	46	42	22
Acetic acid,	$C_2H_4O_2$	60	64	22
Propionic acid,	$C_3H_6O_2$	74	86	22
Butyric acid,	$C_4H_8O_2$	88	108	22
Valeric acid,	$C_5H_{10}O_2$	102	130	

Hence it follows that the group CH_2 has the specific volume 22.

2. The substitution of 1 atom of carbon for 2 atoms of hydrogen makes no alteration in the specific volume of a liquid compound :

		Mol. Wt.	Specific Volume.
Octane,	C_8H_{18}	114	187
Cymene,	$C_{10}H_{14}$	134	187
Ethylic ether,	$C_4H_{10}O$	74	106·8
Phenol,	C_6H_6O	94	106·8

Now, since the specific volume of CH_2 is 22, and that of 1 carbon-atom is the same as that of 2 hydrogen-atoms, it follows that the specific volume (or atomic volume) of carbon is 11 and that of hydrogen 5·5.

Calculating in a similar manner the specific volume of oxygen in various carbon-compounds, it is found that this element has two specific or atomic volumes, accordingly as it is united by both its units of affinity to one carbon-atom, as in the group $C{=}O$, in which case its specific volume is 12·2 ; or to two different atoms, as in methyl alcohol, $O<\begin{matrix}CH_3\\H\end{matrix}$, and methyl ether, $O<\begin{matrix}CH_3\\CH_3\end{matrix}$, in which case the specific volume is 7·8. In acetic acid,  $\begin{matrix}CH_3\\ |\\ O{=}C{-}O{-}H\end{matrix}$, the O-atom which is connected with a carbon-atom alone has the specific volume 12·2, while that joined to both C and H has the specific volumes 7·8. If this compound be represented as acetyl-hydroxide, $\left.\begin{matrix}CH_3CO\\ H\end{matrix}\right\}O$, or $\left.\begin{matrix}C_2H_3O\\ H\end{matrix}\right\}O$, that is to say as water in which 1 atom of hydrogen is replaced be the radicle acetyl, C_2H_3O, we may say that the specific volume of the intra-radical oxygen is 12·2, and that of the extra-radical oxygen 7·8.

The specific volume of dyad sulphur varies in a similar manner, being 28·6 or 23 accordingly as the sulphur-atom is united to one atom of another element by both its combining units, or to two separate atoms, as in thiocarbonic acid, $\left.\begin{matrix}CS\\ H^2\end{matrix}\right\}S^2$, or $S{=}C{<}\begin{matrix}S{-}H\\ S{-}H\end{matrix}$, where the sulphur-atom united with the C alone has the specific volume 28·6, and the two others, each of which is connected both with C and H, have the specific volume 23.

The specific volume of nitrogen in the amines, *e.g*, H_3C-NH_2 (methyl amine), is 2·3 ; in cyanogen-compounds, 17 ; and in nitroxyl, NO_2, 17·4. The specific volumes of the haloïd elements are the same in all their compounds, viz., Cl = 22·8 ; Br = 27·8 ; I = 37·5.

From these data the specific volumes of compounds may be calculated with very near approach to the values directly obtained by dividing the molecular weights by the specific gravities. A comparison of the observed and calculated values of a few compounds is given in the following table :—

Substance.	Formula.	Specific Volume at the Boiling Point.	
		Calculated.	Quotient of Mol. Wt. by Sp. Gr.
Water............	H_2O	2.5·5+ 7·8 = 18·8	18·8
Methyl alcohol.	$CH_3 . O . H$	11+4.5·5+ 7·8 = 40·8	42
Ethyl alcohol...	$C_2H_5 . O . H$	2.11+6.5·5+ 7·8 = 62·8	62·5
Acetic acid......	$C_2H_3O . O . H$	2.11+4.5·5+ 7·8+12·2 64	63·6
Acetone..........	$CO(CH_3)_2$	3.11+6.5·5+ 12·2 = 78·2	77·6
Butyric acid	$C_4H_7O . OH$	4.11+8.5·5+ 7·8+12·2 =108	107
Ethyl acetate ...	$C_2H_3O . O . C_2H_5$	4.11+8.5·5+ 7·8+12·2 =108	107·6
Mercaptan	$C_2H_5S . H$	2.11+6.5·5+ 23 78	76·1
Aniline	$C_6H_5 . NH_2$	6.11+7.5·5+ 2·3 =106·8	106·8
Ethyl cyanide..	$C_2H_5 . CN$	3.11+5.5·5+17 = 77·5	77·2
Ethyl nitrate....	$C_2H_5 . O . NO_2$	2.11+5.5·5+17·4+3.7·8= 90·3	90·1
Chloroform......	$CHCl_3$	11 5.5 + 3.2 2.8 = 84·9	84·8
Ethyl bromide..	C_2H_5Br	2.11+5.5·5+27·8 = 77·3	78·4
Ethyl Iodide ...	C_2H_5I	2.11+5.5·5+37·5 = 87·0	86·4

Melting Point and Boiling Point.—Solid carbon-compounds are for the most part capable of melting without decomposition, and exhibit fixed melting points. Many of those which are liquid at ordinary temperatures boil and volatilise without decomposition under the ordinary atmospheric pressure, and their boiling temperatures are constant under any given pressure. Many others, on the contrary, when heated under the ordinary pressure, decompose before they boil, but some of these are found to boil without decomposition under pressures more or less reduced.

Generally speaking, the boiling point of a compound is higher as its constitution is more complex. This is seen (1) in polymeric compounds: for example, formic aldehyde, CH_2O, is a gas; but acetic acid, $C_2H_4O_2$, is a liquid boiling at 118°; lactic acid, $C_3H_6O_3$, boils at 200°, but at the same time decomposes to a great extent; and grape-sugar, $C_6H_{12}O_6$, is not volatile at all, but undergoes complete decomposition when strongly heated.

2. In the successive terms of a homologous series, the boiling point rising successively for every addition of CH_2. In some cases this increase is very regular: thus in the series of normal alcohols,* $C_nH_{2n+2}O$, the successive members, up to the 8-carbon alcohol, differ in boiling point by nearly 19°, and in the normal fatty acids, $C_nH_{2n}O_2$, the difference from the second to the sixth term is very nearly 22°, but afterwards becomes less; as shown by the following table:—

Alcohols, $C_nH_{2n+2}O$.			Acids, $C_nH_{2n}O_2$.		
Ethylic,	C_2H_6O	78·4°	Acetic,	$C_2H_4O_2$	118°
Propylic,	C_3H_8O	97°	Propionic,	$C_3H_6O_2$	140·6°
Butylic,	$C_4H_{10}O$	116°	Butyric,	$C_4H_8O_2$	163·2°
Pentylic,	$C_5H_{12}O$	137°	Valeric,	$C_5H_{10}O_2$	184·5°
Hexylic,	$C_6H_{14}O$	156·6°	Caproic,	$C_6H_{12}O_2$	204·5°
Heptylic,	$C_7H_{16}O$	177°	Oenanthylic,	$C_7H_{14}O$	223–224°
Octylic,	$C_8H_{18}O$	190–192°	Rutic,	$C_8H_{16}O_2$	232–234°
Nonylic,	$C_9H_{20}O$	200°	Pelargonic,	$C_9H_{18}O_2$	253–254°

In other cases, the differences between the boiling points of the successive members of a series decrease by a regular amount up to a certain term, beyond which they become constant. Thus, in the normal paraffins, C_nH_{2n+2}, the differences decrease regularly by about 4° till a constant difference of 19° is attained; thus:

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* Normal carbon-compounds are those in which all the carbon-atoms are linked together in a single chain, *e.g.*, normal butyl alcohol, $CH_3—CH_2—CH_2—CH_2OH$. (See HYDROCARBONS, ALCOHOLS, &c.)

		Boiling Point.	Difference.
Butane,	C_4H_{10}	1°	
Pentane,	C_5H_{12}	38°	37°
Hexane,	C_6H_{14}	70°	32°
Heptane,	C_7H_{16}	99°	29°
Octane,	C_8H_{18}	124°	25°
Dodecane,	$C_{12}H_{26}$	202°	4 × 19°
Hexdecane,	$C_{16}H_{34}$	278°	4 × 19°

In the haloïd ethers and acetic ethers of the alcohol-radicles, C_nH_{2n+1}, the differences of boiling point decrease by about 2°, as shown in the following table:—

Radicles.		Chlorides, $C_nH_{2n+1}Cl$.	Bromides, $C_nH_{2n+1}Br$.	Iodides, $C_nH_{2n+1}I$.	Acetates, $C_nH_{2n+1}.C_2H_3O_2$.
Methyl,	CH_3	...	...	40°	...
Ethyl,	C_2H_5	12·5°	39°	72°	74°
Propyl,	C_3H_7	46·4°	71°	102°	102°
Butyl,	C_4H_9	77·6°	100·4°	129·6°	125·1°
Pentyl,	C_5H_{11}	105·6°	128·7°	153·4°	148·4°
Hexyl,	C_6H_{13}	...	...	179·4°	168·7°
Octyl,	C_8H_{17}	180°	199°	221°	207°

Metameric compounds containing similarly constituted radicles boil for the most part at nearly equal temperatures, *e.g.*,

Formula, $C_6H_{12}O_2$.	Boiling Point.
Butyl acetate,	124·5°
Propyl propionate,	122·4°
Ethyl butyrate,	121·6°

Formula, $C_7H_{14}O_2$.	Boiling Point.
Pentyl acetate,	148·4°
Butyl propionate,	146·0°
Propyl butyrate,	143·4°

Those, on the other hand, which contain differently constituted radicles, boil at different temperatures, the boiling point being lower as the compound has a more complex constitution, or, in other words, as it contains a greater number and variety of radicles: in the butyl alcohols, for example:

		Boiling Point.
Normal butyl alcohol,	$C_4H_9.OH$	116°
Isobutyl alcohol,	$C_2H_3(CH_3)_2.OH$	108°
Secondary butyl alcohol,	$(CH_3)(C_2H_5)CH.OH$	96°
Tertiary butyl alcohol,	$C(CH_3)_3.OH$	92°

Subtraction of hydrogen generally raises the boiling point, *e.g.*,

Heptane, C_7H_{16}	Heptene, C_7H_{14}	Heptine, C_7H_{12}
99°	100°	107°

Hydrocarbons always boil at lower temperatures than their substitution-derivatives, the boiling point rising in proportion as a greater amount of hydrogen is displaced.

Ethane, C_2H_6 gas.	Ethyl chloride, C_2H_5Cl 12°	Ethene chloride, $C_2H_4Cl_2$ 82·5°	
	Ethyl alcohol, $C_2H_5.OH$ 78·4°	Ethene alcohol, $C_2H_4(OH)_2$ 197·5°	
	Acetic acid, $C_2H_3O.OH$ 118°	Chloracetic acid, $C_2H_2ClO.OH$ 186°	
Benzene, C_6H_6 82°	Chlorobenzene, C_6H_5Cl 135°	Dichlorobenzene, $C_6H_4Cl_2$ 172°	Trichlorobenzene, $C_6H_3Cl_3$ 210°
	Amidobenzene, $C_6H_5(NH_2)$ 182°	Diamidobenzene, $C_6H_4(NH_2)_2$ 287°	

OPTICAL PROPERTIES.

Refractive Power.—In the chapter on LIGHT (i. 72) it has been explained that the index of refraction of any transparent substance, that is to say, the ratio of the sine of the angle of incidence to the sine of the angle of refraction, is a constant quantity, so long as the density of the substance remains constant:—

$$\frac{\sin i}{\sin r} = n.$$

With variation of density (d), and therefore also with variation of temperature, the index of refraction likewise varies; but it has been found, by exact observation made on a large number of substances at different temperatures, that the quantity

$$\frac{n-1}{d},$$

called the specific refractive energy, is constant for all temperatures; and this quantity multiplied by the molecular weight of the substance, gives the molecular refractive energy or refraction-equivalent.

The relations between chemical composition and refractive energy have been studied chiefly in bodies of the fatty group (methane-derivatives), and the following general laws have been established:—

1. *Isomeric bodies have in many instances equal refraction-equivalents.*

2. *In compounds belonging to the same homologous series, the refraction-equivalent increases, in all cases, for a difference of* CH_2, *by a nearly equal amount; the mean increment in the fatty alcohols and acids, &c., being* 7·60.

3. *The refraction-equivalent of a mixture or compound is equal to the sum of the refraction-equivalents of its components.*

This last law gives the means of determining the refraction-equivalents of elements from those of their compounds, the method of calculation being similar to that adopted in the determination of the specific volumes of the elements (p. 32). In the homologous fatty alcohols and acids, the mean values of the refraction-equivalents of carbon, hydrogen, and oxygen are found to be—

C	H	O
5·00	1·30	3·00

By means of these values the refraction-equivalent of a compound of carbon, hydrogen, and oxygen, may be calculated from the formula

$$R = mr + m'r' + m''r'',$$

where m, m', m'', denote the numbers of atoms of the three elements, and r, r', r'', their refraction-equivalents.

Thus, for ethyl-alcohol, C_2H_6O, the calculated value is

$$2 \times 5 + 6 \times 1·3 + 3 = 20·8.$$

On the other hand, direct observation gives

$$d = 0·7964 ; \quad n = 1·3606 : \text{therefore } \frac{n-1}{d} = 0·4526 ;$$

and multiplying this number by 46, the molecular weight of alcohol, we obtain for the refraction-equivalent the number 20·8, agreeing exactly with the calculated value.

In like manner for acetic acid, $C_2H_4O_2$, we have

$$2 \times 5 + 4 \times 1·3 + 2 \times 3 = 21·2,$$

and for the direct determination—

$$d = 1·053 ; \quad n = 1·372 ; \quad \text{mol. wt.} = 60.$$

Therefore— $\frac{n-1}{d} \times 60 = 0·3533 \times 60 = 21·2.$

The specific refractive energy of a mixture is the mean of that of its constituents, so that if we know what compounds are present in a mixture, the determination of the specific refractive energy of the mixture (those of the components being known) affords the means of estimating the quantity of each. For example, a mixture of 81·3 per cent. amyl alcohol, $C_5H_{12}O$, and 18·7 ethyl alcohol, C_2H_6O, was found to have an index of refraction which gave $\frac{n-1}{d} = 0·4940$. Now the mode of calculation above explained gives for ethyl alcohol $\frac{n-1}{d} = 0·4528$, and for amyl alcohol, 0·5033. Hence, putting x and y for the relative quantities of ethyl and amyl alcohols in the mixture, we have the two equations—

$$x + y = 100$$
$$0·4528\,x + 0·5033\,y = 49·4 ;$$

whence $x = 18{\cdot}4$; $y = 81{\cdot}5$, values agreeing very nearly with the quantities actually mixed.

This method of optical analysis affords a convenient method of determining the proportions in which any two substances are mixed, in cases when a separation of the two cannot easily be effected by chemical or physical means, as when they differ but slightly in boiling point, solubility, or other quality which might otherwise be available for their separation.

The composition of chemical compounds may, in many cases, be determined in a similar manner.

In certain series of carbon-compounds, viz., the hydrocarbons of the aromatic group, including benzene, C_6H_6, and its homologues,—in the series of organic bases homologous with pyridine, C_5H_5N, and chinoline, C_9H_7N,—and in certain oxidised essential oils, the refraction-equivalents are found to be considerably higher than those calculated as above from the values of the elements. The deviations from the normal values exhibit a certain regularity, depending on the composition, which, for the typical hydrocarbons of the several series, may be represented as follows :

		Refraction-equivalent.	
Paraffins,	C_nH_{2n+2}	Normal	
Olefines,	C_nH_{2n}	„	
Terpenes,	$C\ H_{2n-4}$	„	+ 3
Benzene and its homologues,	C_nH_{2n-6}	„	+ 6
Naphthalene,	$C_{10}H_8$	„	+14
Anthracene,	$C_{14}H_{10}$	„	+17

Similar relations are exhibited by a series of oxidised compounds, differing from one another only in their amount of hydrogen:

Peppermint camphor,	$C_{10}H_{20}O$	Normal	
Dihydrate of cajputene,	$C_{10}H_{18}O$	„	
Wormwood oil,	$C_{10}H_{16}O$	„	+ 1
Carvol,	$C_{10}H_{14}O$	„	+ 6
Anethol,	$C_{10}H_{12}O$	„	+13

Circular Polarisation.—The power of turning the plane of polarisation of a ray of light to the right or to the left, possessed by many carbon-compounds, even in the liquid state or in solution, has already been mentioned in the chapter on LIGHT (i. 83), which also contains a description and figure of an instrument used for measuring the amount of this power. Substances possessing this power are said to be optically active, or to possess optical rotatory power, dextro- or lævo-; such are amyl alcohol, turpentine oil, camphor, various kinds of sugar, and several vegetable acids and alkaloïds.

The angle of rotation (α) for any particular ray of the spectrum the line D, for example—produced by any particular liquid, is proportional to the length of the column of liquid traversed by the ray, and to the quantity of active substance contained in it; and the quantity $[\alpha]$, given by the expression

$$[\alpha] = \frac{\alpha}{\varepsilon\delta l},$$

in which α is the observed angle of rotation, ε the weight of substance in 1 gram of the solution, δ the specific gravity of the solution, and l the length of the column (in decimeters), is called the specific rotatory power. It is constant for each substance at a given temperature.

For example, by dissolving 11·347 grams of grape-sugar in 88·653 grams of water, a solution is obtained, having a specific gravity of 1·048, and producing in a tube 2 decimeters long, a rotation of 13·7°. Hence the molecular rotatory power of grape-sugar is given by the equation,

$$[\alpha] = \frac{13{\cdot}7}{0{\cdot}11347 \times 2 \times 1{\cdot}048} = 57{\cdot}6.$$

The power of circular polarisation appears to depend on a certain want of symmetry in the molecules of the active substance, and in crystallised bodies it is usually associated with the existence of hemihedral faces. This connection is strikingly exhibited by the isomeric bodies, tartaric and racemic acid, $C_4H_6O_6$. Racemic acid, the crystals of which are holohedral, has no action or polarised light; but by certain processes to be explained hereafter (see TARTARIC ACID), it may be separated into two isomeric acids, called dextro- and lævo-tartaric acids, the former of which (ordinary tartaric acid) turns the plane of polarisation to the right, the latter to the left; and the crystals of these acids are perfectly similar in form, excepting that they possess certain hemihedral faces, occupying opposite positions on the crystal, so that the two crystals are not superposible, but are related to one another like the two hands, or the two sides of the face, or an object and its reflected image. Moreover, the union of the these two oppositely active tartaric acids reproduces racemic acid with its original properties, optically inactive, and forming holohedral crystals.

Artificially prepared carbon-compounds are, for the most part, active or inactive, according to the character of the compounds from which they are derived. Thus malic acid, prepared by the action of hydriodic acid on tartaric acid, or by that of nitrous acid on asparagin or on optically active aspartic acid, is itself optically active, like the malic acid of fruits; but inactive aspartic acid heated with nitrous acid, yields a malic acid which has no action on polarised light. Recently, however, it has been found that inactive tartaric acid may be converted by a strong heat into dextro-tartaric acid.

Methane-Derivatives, or Fatty Group.

HYDROCARBONS.

FIRST SERIES, C_nH_{2n+2}.—PARAFFINS.*

THIS series, as already observed, consists of saturated hydrocarbons. The names and formulæ of the first six are given in the table on page 22; the following terms may be called, *heptane, octane, nonane, decane, endecane, dodecane,* &c.

Occurrence and Formation.—Many of the paraffins occur ready-formed in American petroleum and other mineral oils of similar origin. They are formed artificially by the following processes:

1. By the simultaneous action of zinc and water on the alcoholic iodides (p. 24), compounds derived from these same hydrocarbons by the substitution of one atom of iodine for hydrogen.

This reaction, which appears to be applicable to the formation of the whole series of paraffins, is represented by the general equation:

$$\underset{\text{Alcoholic iodide.}}{2C_nH_{2n+1}I} + Zn_2 + 2H_2O = ZnH_2O_2 + ZnI_2 + \underset{\text{Paraffin.}}{2C_nH_{2n+2}}$$

As an example, we may take the formation of ethane from ethyl iodide:

$$2C_2H_5I + Zn_2 + 2H_2O = ZnH_2O_2 + ZnI_2 + 2C_2H_6.$$

2. All the paraffins may be produced by heating the alcoholic iodides with zinc alone. Generally speaking, however, two of these hydrocarbons are obtained together, the first product of the reaction being a paraffin containing twice as many carbon-atoms as the alcoholic iodide employed; and this compound being then partly resolved into the paraffin containing half this number of carbon-atoms, and the corresponding olefine, C_nH_{2n}; thus:

$$\underset{\text{Ethyl iodide.}}{2C_2H_5I} + Zn = ZnI_2 + \underset{\text{Quartane.}}{C_4H_{10}}$$

and

$$\underset{\text{Quartane.}}{C_4H_{10}} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Ethane.}}{C_2H_6}$$

---

* From *parum affinis,* indicating their chemical indifference. The name paraffin has long been applied to the solid compounds of the series, on account of this character; and many of the liquid compounds of the same series are known commercially as *paraffin oils.* It is convenient, therefore, to employ the term paraffin as a generic name for the whole series.

Generally:

$$2C_nH_{2n+1}I \quad + \quad Zn \quad = \quad ZnI_2 \quad + \quad C_{2n}H_{4n+2}$$

and,

$$C_{2n}H_{4n+2} \quad = \quad C_nH_{2n} \quad + \quad C_nH_{2n+2}.$$

3. By the electrolysis of the fatty acids ($C_nH_{2n}O_2$). For example, a solution of potassium acetate, divided into two parts by a porous diaphragm, yields pure hydrogen, together with potash, at the negative electrode, and at the positive electrode (if of platinum) a mixture of carbon dioxide and ethane gases:

$$2C_2H_4O_2 \quad = \quad 2CO_2 \quad + \quad C_2H_6 \quad + \quad H_2.$$

We may suppose that the two molecules of acetic acid are resolved by the current into H_2 and $C_4H_6O_4$, and that the latter then splits up into $2CO_2$ and C_2H_6. The general reaction is:

$$2C_nH_{2n}O_2 \quad = \quad 2CO_2 \quad + \quad C_{2n-2}H_{4n-2} + H_2.$$

4. Some of the paraffins are obtained from the acids of the series $C_nH_{2n}O_2$ and $C_nH_{2n-2}O_4$, by the action of alkalis, which abstract carbon dioxide from those acids, the hydrocarbon thus eliminated containing one or two atoms of carbon less than the acid from which it is produced. In this manner methane (marsh gas) is obtained by heating potassium acetate with potassium hydroxide (i. 172).

$$C_2H_3O_2K \quad + \quad HKO \quad = \quad CO_3K_2 \quad + \quad CH_4.$$

Also hexane and octane, by similar treatment of the potassium salts of suberic acid, $C_8H_{14}O_4$, and sebacic acid, $C_{10}H_{18}O_4$:

$$\underset{\text{Suberate.}}{C_8H_{12}O_4K_2} \quad + \quad 2HKO \quad = \quad 2CO_3K_2 \quad + \quad \underset{\text{Hexane.}}{C_6H_{14}}$$

$$\underset{\text{Sebate.}}{C_{10}H_{16}O_4K_2} \quad + \quad 2HKO \quad = \quad 2CO_3K_2 \quad + \quad \underset{\text{Octane.}}{C_8H_{18}}$$

Generally speaking, however, a further decomposition takes place, resulting in the formation of hydrocarbons containing a smaller proportion of hydrogen than the paraffins.

5. The paraffins may also be produced from the olefines, C_nH_{2n}, by combining the latter with bromine, and heating the resulting compound, $C_nH_{2n}Br_2$, with a mixture of potassium iodide, water, and metallic copper. The bromine-compound is then decomposed, and the hydrocarbon, C_nH_{2n}, is partly reproduced in the free state, partly converted, by addition of hydrogen, into a paraffin.

6. Several of the paraffins are produced by the dry or destructive distillation of butyrates and acetates.

7. They are also found amongst the products of the dry dis-

tillation of coal, especially Boghead and Cannel coal, and, as already observed, they constitute the principal portion of many mineral oils, called *petroleum*, *naphtha*, or *rock-oil*, formed by the gradual decay or decomposition of vegetable matter beneath the earth's surface. By far the largest quantities of these oils are obtained from Canada, Pennsylvania, and other parts of North America. Abundant petroleum springs exist, also, on the north-west of the Caspian Sea, near Baku, at Rangoon in Burmah, and in various parts of Italy. The American petroleum consists almost wholly of paraffins. Burmese tar contains, also, small quantities of hydrocarbons belonging to other series, especially homologues of benzene.

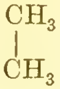
Properties and Reactions of the Paraffins.—Methane, ethane, propane, and butane are gaseous at ordinary temperatures; most of the others are liquids, regularly increasing in specific gravity, viscidity, boiling point, and vapour-density, as their molecular weight becomes greater; those containing 20 carbon-atoms or more are crystalline solids.

The paraffins are saturated hydrocarbons, incapable of uniting directly with monatomic elements or radicles, but they easily yield substitution-derivatives. When subjected to the action of *chlorine* or *bromine*, they give up a part, or in some cases the whole, of their hydrogen in exchange for the halogen element. Thus equal volumes of chlorine and methane, CH_4, exposed to diffused daylight, yield the compound CH_3Cl, called chloromethane or methyl chloride; and, by further subjecting this product to the action of an excess of chlorine in direct sunshine, it may be successively converted into the more highly chlorinated compounds CH_2Cl_2, $CHCl_3$, CCl_4. Ethane, C_2H_6, also yields, by a series of processes to be presently described, the products C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6; and similarly for the other compounds of the series. These bodies, which may be regarded as compounds of chlorine and other halogen elements with the radicles $(CH_3)'$, $(CH_2)''$, $(CH)'''$, &c., are called haloïd ethers. When treated with water or aqueous alkalis, they exchange the haloïd element for an equivalent quantity of hydroxyl, (HO), thereby producing alcohols (p. 25); and, on the other hand, they may be formed from the alcohols by the action of the chlorides, bromides, and iodides of hydrogen or phosphorus.

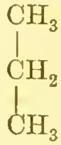
Nitric acid attacks the higher members of the paraffin series, forming nitro-compounds; octane, C_8H_{18}, thus treated, yields the compound, $C_8H_{17}(NO_2)$. The lower paraffins, on the other hand, are not affected by nitric acid; but by indirect means compounds may be formed, having the composition of paraffins in which the hydrogen is more or less replaced by nitryl: for example, *nitro-methane*, $CH_3(NO_2)$; *trinitromethane* or *nitroform*, $CH(NO_2)_3$.

The first three hydrocarbons of the series, viz., CH_4, C_2H_6, C_3H_8, exhibit exactly the same physical and chemical properties in whatever way they may be prepared; and indeed the constitutional formulæ of these bodies, viz.

CH_4



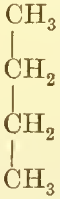
$$\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$$



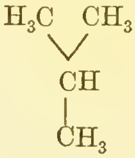
$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

show that they are not susceptible of isomeric modifications, inasmuch as there is but one way in which the carbon-atom in either of them can be grouped; in ethane each carbon-atom is directly combined with three hydrogen-atoms and the other carbon-atom; and whether we regard it as ethyl hydride, $H—CH_2CH_3$, or as dimethyl, $H_3C—CH_3$, this arrangement remains the same. In propane, C_3H_8, each carbon-atom is directly combined with at most two other carbon-atoms, and there is no other way in which the atoms can be arranged.

But if we look at the formula of the 4-carbon paraffin, C_4H_{10}, we see that it may be written in either of the following forms:



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$



in the first of which, neither of the carbon atoms is directly united with more than two others, whereas, in the second, one of the carbon-atoms is directly combined with three others. The first may be represented, either as *propyl-methane*, $C\left\{\begin{array}{l} CH_2CH_2CH_2 \\ H_3 \end{array}\right.$ = $C\left\{\begin{array}{l} CH_2C_2H_5 \\ H_3 \end{array}\right. = C\left\{\begin{array}{l} C_3H_7 \\ H_3 \end{array}\right.$, or as *diethyl*, $H_5C_2.C_2H_5$, according to the manner in which we may suppose it to be divided; the second as *trimethyl-methane*, $C\left\{\begin{array}{l} (CH_3)_3 \\ H \end{array}\right.$, or as *isopropyl-methane*, $C\left\{\begin{array}{l} CH(CH_3)_2 \\ H_3 \end{array}\right.$, the radicle $CH(CH_3)_2$ being called isopropyl, to distinguish it from normal propyl, $CH_2(C_2H_5)$.

A comparison of the modes of formation and decomposition of all the paraffins which have been obtained by definite reactions shows that they may be arranged in the four following groups:[*]

1. Normal Paraffins, in which each carbon-atom is directly connected with, at most, *two* other carbon-atoms, or which contain the group or residue CH_2 (methene), associated with two monatomic alcohol-radicles, C_nH_{2n+1}, *e.g.*,

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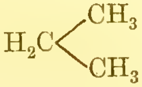
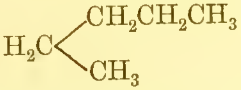
[*] Schorlemmer, Proceedings of the Royal Society, xvi. 34, 367.

Dimethyl-methane, $C\left\{\begin{array}{l}CH_3\\CH_3\\\ \ H_2\end{array}\right.$ or

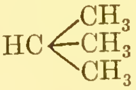


Methyl-propyl methane, $C\left\{\begin{array}{l}C_3H_7\\C\ H^3\\\ \ H_2\end{array}\right.$ or

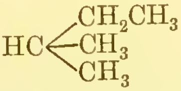


2. Isoparaffins, in which one carbon-atom is directly united with *three* other carbon-atoms, or in which the trivalent group or residue, CH (methenyl) is associated with three monatomic radicles, C_nH_{2n+1}, *e.g.*,

Trimethyl-methane, $C\left\{\begin{array}{l}(CH_3)_3\\\ \ \ H\end{array}\right.$ or

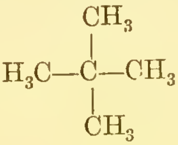


Ethyldimethyl-methane, $C\left\{\begin{array}{l}C_2H_5\\(CH_3)_2\\\ \ \ H\end{array}\right.$ or



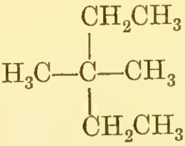
3. Neoparaffins, in which one carbon-atom is directly united with *four* other carbon-atoms, or, in other words, with four monatomic radicles, C_nH_{2n+1}, *e.g.*,

Tetramethyl-methane, $C(CH_3)_4$ or



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

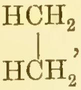
Dimethyl-diethyl-methane, $C\left\{\begin{array}{l}(C_2H_5)_2\\(CH_3)_2\end{array}\right.$ or



$$H_3C-\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{C}}-CH_3$$

The paraffins of these three classes are constructed on the methane type.

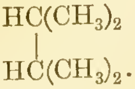
4. Mesoparaffins, in which two methenyl groups, having their carbon-atoms linked together by one combining unit, are each associated with *two* monatomic radicles, C_nH_{2n+1}. These paraffins are, therefore, constructed on the ethane type,



$$\begin{array}{c}HCH_2\\|\\HCH_2\end{array}$$

, *e.g.*:

Tetramethylethane, . .



$$\begin{array}{l}HC(CH_3)_2\\\ \ |\\HC(CH_3)_2.\end{array}$$

The paraffins of the first and second class have for some time been distinguished as *normal* and *iso-paraffins*, and Dr. Odling has lately proposed to distinguish the third class by the prefix *neo* (from νεος, new, as being the latest discovered), and the fourth by the prefix *meso*, intimating their intermediate character, as associated with the iso-paraffins in containing the residue CH, and with the neoparaffins in containing four alcohol-radicles.* He also suggests an abbreviated notation, consisting in the use of the Greek letters σ, ν, and μ, as indices of the iso-, neo-, and meso-paraffins respectively, for example:

$$\begin{array}{cccc} C_6H_{14} & C_6H_{14}^{\sigma} & C_6H_{14}^{\nu} & C_6H_{14}^{\mu} \\ \text{Hexane.} & \text{Isohexane.} & \text{Neohexane.} & \text{Meso-hexane.} \end{array}$$

$$H_2C\left\{\begin{array}{l} CH_2CH_2CH_3 \\ CH_3 \end{array}\right. \quad HC\left\{\begin{array}{l} CH_2CH_2CH_3 \\ CH_3 \\ CH_3 \end{array}\right. \quad C\left\{\begin{array}{l} CH_2CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \end{array}\right. \quad \begin{array}{l} HC\left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\right. \\ \ \ \| \\ HC\left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\right. \end{array}$$

Isomerism in the Substitution-derivatives of the Paraffins.—It has already been stated that the paraffins can exchange one or more of their hydrogen-atoms for various elements and compound radicles, Cl, Br, O, OH, NO_2, &c., giving rise to alcohols and ethers. Confining our attention for the present to the monatomic derivatives, that is to say, those in which 1 atom of hydrogen is replaced by a univalent radicle X, it is obvious that the first two hydrocarbons of the series C_nH_{2n+2}, viz., CH_4 and $\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$, can each give rise to only one derivative containing any particular monatomic radicle, these derivatives being respectively represented by the formulæ—

$$CH_3X \qquad \text{and} \qquad \begin{array}{l} CH_3 \\ | \\ CH_2X \end{array}$$

for supposing, as is most probable, that all the hydrogen-atoms have the same value, and are attached to their respective carbon-atoms in the same way, the result of the substitution must be the same, whichever of these hydrogen-atoms may be thus replaced. But with all the paraffins containing more than two atoms of carbon, the case is different. Thus, in propane, $CH_3—CH_2—CH_3$, the substitution may take place either in one of the exterior groups CH_3, or in the middle group CH_2, giving rise to two derivatives of different structure, distinguished by the terms primary and secondary, viz.,

$$\begin{array}{lcl} \text{Primary.} & \qquad & \text{Secondary.} \\ CH_2X & & CH_3 \\ | & & | \\ CH_2 & & CHX \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

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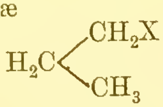
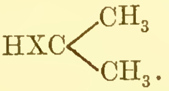
* Philosophical Magazine [5], i. 205.

In the primary derivative, the carbon-atom joined to the radicle X is connected immediately with only one other carbon-atom; in the secondary derivative, it is linked to two other carbon-atoms. These are the only possible modifications of a monatomic derivative of the 3-carbon paraffin C_3H_8; they may be more shortly represented by the formulæ



$$H_2C\begin{matrix}\diagup CH_2X\\ \diagdown CH_3\end{matrix}$$

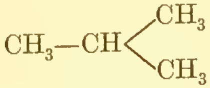


$$HXC\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}.$$

The 4-carbon paraffin, butane, admits of a greater number of modes of substitution. In the first place, the hydrocarbon itself is susceptible of two modifications, viz.,

$$CH_3—CH_2—CH_2—CH_3$$

Normal butane.



$$CH_3—CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

Isobutane or
Trimethyl-methane.

From the first may be formed one primary and one secondary derivative, these terms having the meaning above explained; while the second yields another primary derivative, and likewise a *tertiary* derivative, in which the carbon-atom joined to the radicle X is joined also to three other atoms of carbon. These four derivatives are represented by the following formulæ:—

Primary,	Normal	$CH_3—CH_2—CH_2—CH_2X$	or	$H_2C\left\{\begin{matrix}C_2H_4X\\CH_3\end{matrix}\right.$
	Iso-	$\begin{matrix}H_3C\\H_3C\end{matrix}\!>CH—CH_2X$	or	$HC\left\{\begin{matrix}CH_2X\\(CH_3)_2\end{matrix}\right.$
Secondary,		$CH_3—CHX—CH_2—CH_3$	or	$HXC\left\{\begin{matrix}C_2H_5\\CH_3\end{matrix}\right.$
Tertiary,		$\begin{matrix}H_3C\\H_3C\end{matrix}\!>CX—CH_3$	or	$XC\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$

The two primary derivatives are distinguished by containing the radicles normal propyl, $CH_3—CH_2—CH_2—$ and isopropyl $—CH(CH_3)_2$ respectively.

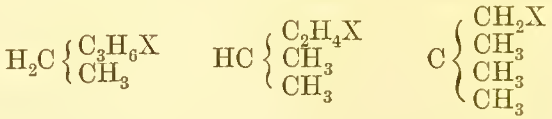
Of the four monatomic butane derivatives, the normal primary and the secondary are derived from normal butane, the iso-primary and the tertiary from isobutane.

The higher paraffins yield a larger number of monatomic derivatives according to the nature of the radicles which enter into their constitution; in other words, according as they are either normal, *i.e.*, have all their carbon-atoms in a single chain, or contain one or more isopropyl groups, $HC<\begin{matrix}CH_3\\CH_3\end{matrix}$; but these derivatives must all be either primary, secondary, or tertiary; for the carbon-atom joined to the radicle X, having one of its combining units thus disposed of, has only three remaining, and cannot therefore be joined to a number of other carbon-atoms greater than three. In other words, the replacement of an H-atom by the radicle X must take place either in a methyl residue, CH_3 a methene residue, CH_2, or a methenyl residue CH, producing respectively a primary, secondary, or tertiary derivative.

Dr. Odling denotes the secondary and tertiary derivatives by the prefixes *pseudo* and *kata*, distinguishing also the latter by the index κ, and the former by the indices π and ψ, according as they contain a normal or an iso-radicle, thus—

Pentyl (C_5H_{11}). Isopentyl ($C_5H_{11}^{\sigma}$). Neopentyl ($C_5H_{11}^{\nu}$).

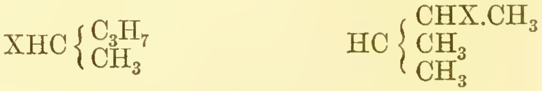
Primary,



$$H_2C\left\{\begin{matrix}C_3H_6X\\CH_3\end{matrix}\right. \qquad HC\left\{\begin{matrix}C_2H_4X\\CH_3\\CH_3\end{matrix}\right. \qquad C\left\{\begin{matrix}CH_2X\\CH_3\\CH_3\\CH_3\end{matrix}\right.$$

Pseudopentyl ($C_5H_{11}^{\pi}$). Pseudisopentyl ($C_5H_{11}^{\psi}$).

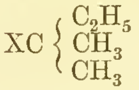
Pseudo,



$$XHC\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right. \qquad HC\left\{\begin{matrix}CHX.CH_3\\CH_3\\CH_3\end{matrix}\right.$$

Katapentyl ($C_5H_{11}^{\kappa}$).

Kata, . .



$$XC\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right.$$

We now proceed to describe the more important of the individual paraffins.

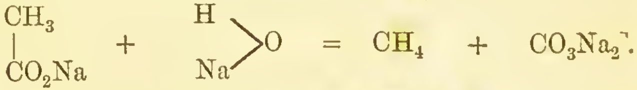
Methane, CH_4, also called *Methyl hydride* and *Marsh gas*, is formed by passing a mixture of hydrogen sulphide and vapour of carbon disulphide over red-hot copper :—

$$2H_2S + CS_2 + 4Cu_2 = CH_4 + 4Cu_2S ;$$

also by the action of water on zinc-methyl :—

$$Zn(CH_3)_2 + H_2O = 2CH_4 + ZnO.$$

The easiest method of preparing it, however, is to heat a mixture of dry sodium acetate and soda-lime (i. 172) :—



$$\begin{matrix}CH_3\\|\\CO_2Na\end{matrix} + \left.\begin{matrix}H\\Na\end{matrix}\right>O = CH_4 + CO_3Na_2.$$

Methane is also produced in the slow decay of vegetable substances, and is found in coal mines as fire-damp, also in marshes and stagnant pools, from which it may be evolved as gas by stirring the mud. Lastly, it is formed by the dry distillation of various organic substances, and forms the chief constituent of coal-gas.

Methane is a colourless inodorous gas which burns with a yellow flame, producing water and carbon dioxide. Its density compared with hydrogen as unity is 8, showing that the molecule CH_4 has the normal 2-volume condensation, $\frac{12+4\times 1}{2} = 8$. When a mixture of equal volumes of methane and chlorine is exposed to sunshine, an explosion takes place, hydrogen chloride being formed, and carbon separated; but in diffused daylight the action goes on slowly, and substitution-products are formed, viz., monochloromethane or methyl chloride, CH_3Cl, and with excess of chlorine, also the compounds, CH_2Cl_2 and $CHCl_3$.

Ethane, C_2H_6 or $H_3C—CH_3$.—This compound, which may also be regarded as *dimethyl*, or as *ethyl hydride*, $C_2H_5.H$ (p. 42), is formed by the general reactions already indicated (p. 39), viz., by the action of zinc and water on ethyl iodide; of zinc alone on the same compound, and on methyl iodide; and by the electrolysis of acetic acid, or rather of its potassium salt. It may be prepared in the pure state by decomposing zinc-ethyl with water, or more easily by heating acetic anhydride with barium dioxide:—

$$2(C_2H_3O)_2O + BaO_2 = C_2H_6 + (C_2H_3O_2)_2Ba + 2CO_2.$$

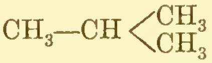
Ethane is a colourless and inodorous gas which has not been liquefied. It is nearly insoluble in water, soluble in about two-thirds of its volume of alcohol. Mixed with an equal volume of chlorine, and exposed to diffused daylight, it forms chlorethane or ethyl chloride, C_2H_5Cl; with excess of chlorine higher substitution-products are formed.

Propane, $C_3H_6 = CH_3—CH_2—CH_3$, also called *Methyl-ethyl*, is one of the constituents of petroleum, and may be produced by the action of zinc and hydrochloric acid on propyl iodide or isopropyl iodide. It is a gas which liquefies at −20°, and dissolves in one-sixth of its volume of alcohol.

Butanes, C_4H_{10}.—Of these compounds, also called *tetranes* or *quartanes*, there are two modifications, viz.:

$$CH_3—CH_2—CH_2—CH_3$$

Normal Butane.



$$CH_3—CH\Big<\begin{matrix}CH_3\\CH_3\end{matrix}$$

Isobutane or Trimethyl-methane.

1. *Normal Butane, Diethyl*, or *Methyl-propyl*, occurs in natural petroleum, and in the distillation-products of Cannel and Boghead coal. It may be formed synthetically by heating ethyl iodide to 100° in sealed tubes with zinc:

$$2C_2H_5I + Zn = ZnI_2 + C_4H_{10}.$$

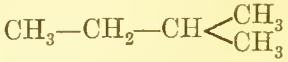
It is a colourless gas, which condenses below 0° to a liquid boiling at +1. Mixed with an equal volume of chlorine, and exposed to light, it yields butyl chloride and other substitution-products.

Isobutane, Trimethyl-methane, or *Methyl-isopropyl*, is formed from tertiary butyl iodide, $(CH_3)_3CI$ (p. 45), by the action of zinc and hydrochloric acid. It is a gas which liquefies at −17°.

Pentanes, C_5H_{12}.—Of these hydrocarbons there are three modifications, viz.:

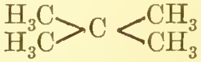
1. Normal Pentane, . $CH_3—CH_2—CH_2—CH_2—CH_3$

2. Isopentane, . .



$$CH_3—CH_2—CH<\begin{array}{l}CH_3\\CH_3\end{array}$$

3. Neopentane, . .



$$\begin{array}{r}H_3C\\H_3C\end{array}>C<\begin{array}{l}CH_3\\CH_3\end{array}$$

1. *Normal Pentane*, or *Ethyl-propyl*, $C_2H_5—C_3H_7$, occurs in petroleum, and in the light oils of Boghead and Cannel coal, but has not been prepared synthetically. It is a liquid of specific gravity 0·6, and boiling at 37–39°. On passing chlorine into its vapour, a primary and a secondary chloride are formed, from which, by a reaction to be hereafter described, the corresponding alcohols may be prepared.

2. *Isopentane* likewise occurs in petroleum, and may be prepared by dehydration of isopentyl alcohol (ordinary amyl alcohol), or by heating the corresponding iodide with water and zinc.

3. *Neopentane*, or *Tetramethyl-methane*, is formed by the action of zinc-methyl on tertiary butyl iodide:

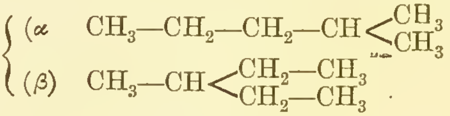
$$2C(CH_3)_3I + Zn(CH_3)_2 = ZnI_2 + 2C(CH_3)_4$$

It is a colourless mobile liquid, which boils at 9·5°, and solidifies at −20° to crystals resembling sal-ammoniac.

Hexanes, C_6H_{14}.—Of these paraffins, five are possible, and four are known:

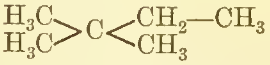
1. Normal Hexane, . $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

2. Isohexane,



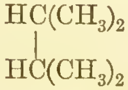
$$\left\{\begin{array}{ll}(\alpha & CH_3—CH_2—CH_2—CH<\begin{array}{l}CH_3\\CH_3\end{array}\\(\beta) & CH_3—CH<\begin{array}{l}CH_2—CH_3\\CH_2—CH_3\end{array}\end{array}\right.$$

3. Neohexane, . .



$$\begin{array}{r}H_3C\\H_3C\end{array}>C<\begin{array}{l}CH_2—CH_3\\CH_3\end{array}$$

4. Mesohexane, . .



$$\begin{array}{l}HC(CH_3)_2\\|\\HC(CH_3)_2\end{array}$$

1. *Normal Hexane*, or *Dipropyl*, occurs in the light oils of Boghead and Cannel coal, and abundantly in Pennsylvanian petroleum. It is formed by the action of sodium on normal propyl iodide, or by that of zinc and hydrochloric acid on secondary hexyl iodide; also by distilling suberic acid with barium oxide:

$$C_8H_{14}O_4 + 2BaO = 2CO_3Ba + C_6H_{14}.$$

It has a density of 0·63 at 17°, and boils at 70–71°.

2. *Isohexane, Propyl-dimethyl-methane*, or *Ethyl-isobutyl*, is formed by the action of sodium on a mixture of ethyl iodide and isobutyl iodide, $CH_2I{-}CH(CH_3)_2$. It has a density of 0·702 at 0°, and boils at 62°.

3. *Neohexane*, or *Ethyl-trimethyl-methane*, produced by the action of zinc-methyl on tertiary butyl iodide, boils at 45°.

4. *Mesohexane*, or *Di-isopropyl*, formed by the action of sodium on isopropyl iodide, $IHC(CH_3)_2$, has a density of 0·677 at 0°, and boils at 58°.

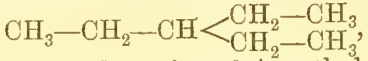
Heptanes, C_7H_{16}. Of these hydrocarbons nine are possible and four are known, viz.:

1. *Normal heptane*, $CH_3{-}(CH_2)_5{-}CH_3$, is contained in Pennsylvanian petroleum, and in the light oils of Boghead and Cannel coal, and may be formed by distilling azelaic acid, $C_9H_{16}O_4$, with barium oxide. It has a density of 0·712 at 16°, and boils at 98°.

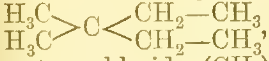
2. *Ethyl-isopentyl*, or *Ethyl-amyl*, $CH_3.CH_2.CH_2.CH_2.CH(CH_3)_2$, a variety of isoheptane, is formed by the action of sodium on a mixture of ethyl-iodide and isopentyl iodide:

$$C_2H_5I + CH_2I.CH_2.CH(CH_3)_2 + Na_2 = 2NaI + C_2H_5.CH_2.CH_2.CH(CH_3)_2$$

It has a density of 0·683 at 18°, and boils at 90°.

3. *Triethyl-methane*,  $CH_3{-}CH_2{-}CH{<}\begin{matrix}CH_2{-}CH_3\\CH_2{-}CH_3\end{matrix}$, another variety of isoheptane, is formed by the action of zinc-ethyl on orthoformic ether (see FORMIC ETHERS).

$$\underset{\text{Orthoformic ether.}}{2CH(OC_2H_5)_3} + \underset{\text{Zinc-ethyl.}}{3Zn(C_2H_5)_2} = \underset{\text{Zinc-ethylate.}}{3Zn(OC_2H_5)_2} + \underset{\text{Triethyl-methane.}}{2CH(C_2H_5)_3}$$

4. *Dimethyl-diethyl-methane*, or *Neoheptane*,  $\begin{matrix}H_3C\\H_3C\end{matrix}{>}C{<}\begin{matrix}CH_2{-}CH_3\\CH_2{-}CH_3\end{matrix}$, is formed by the action of zinc-ethyl on acetone chloride, $(CH_3)_2CCl_2$. It has a density of 0·689 at 27°, and boils at 96°.

The higher paraffins have been but little examined. Normal octane, C_8H_{18}, boiling at 124°, and having a density of 0·703, occurs in petroleum, and is formed—(1) by the action of zinc and hydrochloric acid on normal octyl iodide; (2) by the action of sodium on normal butyl iodide: hence it may be regarded as *dibutyl*, $C_4H_9.C_4H_9$.—*Di-isobutyl*, $(CH_3)_2CH{-}CH_2{-}CH_2{-}CH(CH_3)_2$, obtained by the action of sodium on isobutyl iodide, has a density of 0·705, and boils at 109°.

Di-isopentyl, $C_{10}H_{22}$, obtained from the iodide of isopentyl (ordinary amyl), has a density of 0·770, and boils at 158°.

The paraffins of the higher orders are found, together with those already mentioned, in natural petroleum, and in the light oils obtained by the action of heat on various kinds of coal, especially Boghead and Cannel coal.

In most of these products, however, they are mixed with hydrocarbons belonging to other series; and to separate them from these, the crude petroleum or coal-tar oil is mixed with strong sulphuric acid, which removes the olefines and other non-saturated hydrocarbons, and afterwards with fuming nitric acid, or a mixture of strong nitric and sulphuric acids. The hydrocarbons of the benzene series, and all other compounds except the paraffins, are thereby oxidised or converted into nitro-compounds, which are either dissolved by the acid, or are much less volatile than the hydrocarbons. The oils are then washed with water, dried over caustic potash, and rectified over sodium. The distillate thus obtained consists wholly of paraffins, which are separated by fractional distillation.

When thus purified the petroleum and coal-oil paraffins, which boil between 0° and 130°, are found to consist of two series; those of the first series, which have the higher boiling points, being normal, while those of the second agree for the most part in boiling point with the corresponding synthetically prepared isoparaffins. The boiling points of the two series are as follows :—

		Normal.	Iso.
Butane, . .	C_4H_{10}	0°	...
Pentane, . .	C_5H_{12}	38°	30°
Hexane, . .	C_6H_{14}	69°	61°
Heptane, . .	C_7H_{16}	98°	91°
Octane, . .	C_8H_{18}	124°	118°

The boiling points and specific gravities of the higher paraffins of unknown structure, obtained from the same sources, are as follows :

		Boiling Point.	Specific Gravity.
Nonane, . .	C_9H_{20}	136–138°	0·741 at 15°
Decane, . .	$C_{10}H_{22}$	160–162°	0·757 „ 15°
Endecane, . .	$C_{11}H_{24}$	180–184°	0·765 „ 16°
Dodecane, . .	$C_{12}H_{26}$	196–200°	0·776 „ 20°
Tridecane, . .	$C_{13}H_{28}$	216–218°	0·792 „ 20°
Tetradecane, . .	$C_{14}H_{30}$	236–240°	...
Pentadecane, . .	$C_{15}H_{32}$	255–260°	...

American petroleum likewise yields a quantity of liquid boiling above 300°, and doubtless containing paraffins of still higher order. Some specimens of the crude oil, as it issues from the ground, contain ethane, C_2H_6, and propane, C_3H_8, which are given off from it as gas at ordinary temperatures. In boring for oil also, large quantities of gas escape, exhibiting the characters of methane: hence it is probable that, in the great geological changes which have given rise to the separation of the petroleum, the whole series of paraffins have been formed, from marsh gas upwards.

Solid paraffin is a colourless crystalline fatty substance, probably consisting of a mixture of several of the higher members of the series C_nH_{2n+2}. When heated for some time in a sealed tube, it is resolved, with little or no evolution of gas, into a mixture of olefines and paraffins of lower molecular weight, which remain liquid at ordinary temperatures. This transformation is easily understood: the hydrocarbon, $C_{20}H_{42}$, for example, might be resolved into $C_5H_{12} + C_{15}H_{30}$, or $C_6H_{14} + C_{14}H_{28}$, or $C_7H_{16} + C_{13}H_{26}$, &c., the general equation of the decomposition being,

$$\underset{\text{Paraffin.}}{C_nH_{2n+2}} = \underset{\text{Paraffin.}}{C_{n-p}H_{2(n-p)+2}} + \underset{\text{Olefine.}}{C_pH_{2p}}.$$

The product actually obtained is a mixture of several paraffins and several olefines.*

Paraffin is found native in the coal-measures, and other bituminous strata, constituting the minerals known as *fossil wax*, *ozocerite*, *hatchettin*, &c. It exists also in the state of solution in many kinds of petroleum, and may be separated by distilling off the more volatile portions, and exposing the remainder to a low temperature. In a similar manner also may solid paraffin be obtained from the tar of wood, coal, and bituminous shale. It was first prepared by Reichenbach from wood-tar. It is tasteless and inodorous, insoluble in water, slightly soluble in alcohol, freely in ether, and miscible in all proportions, when melted, with fixed or volatile oils. It burns with a very bright flame, and those varieties of it which melt at temperatures above 45° C. (113° F.) are very hard, and well adapted for making candles. Paraffin is largely used also as a substitute for sulphur for dipping matches; and Dr. Stenhouse has patented its application to woollen cloths, to increase their strength and make them waterproof. More extensive, however, are the uses of the liquid compounds of the paraffin series, known in commerce as *paraffin oil*, *photogene*, *solar oil*, *eupione*, &c. These oils are largely used for burning in lamps; and, when mixed with fatty oils, such as rape and cotton-seed oils, form excellent materials for lubricating machinery. For the former purpose they are exceedingly well adapted, as, with a proper supply of air, they give a much brighter light than that obtained from fatty oils containing oxygen, and are much cleaner in use.

It is necessary to observe, however, that natural petroleum and the oils obtained by the dry distillation of coal, &c., at low temperatures, are mixtures of a great number of paraffins differing greatly in volatility, and that to render them safe for burning in lamps of ordinary construction, they must be freed by distillation from the more volatile members of the series; otherwise they will take fire too easily, and when they become heated, will give off highly inflammable vapours, which, mixing with the air in the body of the lamp, may easily produce dangerously explosive mixtures; serious accidents have indeed arisen from this cause. It has been found by experience that it is not safe to use paraffin oil which will take fire on the application of a match and burn continuously, at a temperature below 100° F.

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* Thorpe and Young (Berichte der deutschen chemischen Gesellschaft, 1872, p. 536).

SECOND SERIES, C_nH_{2n}.—OLEFINES.

The hydrocarbons of this series are polymeric, as well as homologous with one another, inasmuch as their formulæ are all exact multiples of that of the lowest, CH_2. The lower members of the series are gaseous at ordinary temperatures, the higher members are solid, and the intermediate compounds liquid. The names and formulæ of the known members of the olefine series are given in the following table :—

Ethene or Ethylene, ...	C_2H_4
Propene or Propylene, ...	C_3H_6
Tetrene, Butene, or Butylene, . . .	C_4H_8
Pentene or Amylene, ...	C_5H_{10}
Hexene or Hexylene, ...	C_6H_{12}
Heptene or Heptylene, ...	C_7H_{14}
Octene or Octylene, ...	C_8H_{16}
Nonene or Nonylene, ...	C_9H_{18}
Decene or Paramylene, . . .	$C_{10}H_{20}$
Hexdecene or Cetene, ...	$C_{16}H_{32}$
Cerotene, ...	$C_{27}H_{54}$
Melene or Melissene, ...	$C_{30}H_{60}$

Methene, CH_2, the lowest term of the series, does not appear to be capable of existing in the separate state.

Formation of the Olefines.—1. By abstraction of the elements of water from the alcohols of the series $C_nH_{2n+2}O$, homologous with common alcohol, under the influence of powerful dehydrating agents, such as oil of vitriol, phosphoric oxide, or zinc chloride ; thus :—

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Ethene.}}{C_2H_4}$$

2. By heating the monatomic haloïd ethers, $C_nH_{2n+1}Br$, &c., with alcoholic solution of potash, or by passing their vapours over lime at a dull red heat :—

$$\underset{\text{Ethyl bromide.}}{C_2H_5Br} + KOH = \underset{\text{Ethene.}}{C_2H_4} + H_2O + KBr.$$

$$\underset{\text{Pentyl chloride.}}{2C_5H_{11}Cl} + CaO = \underset{\text{Pentene.}}{2C_5H_{10}} + H_2O + CaCl_2.$$

The secondary and tertiary alcohols, and their haloïd ethers are converted into olefines, by this and the preceding reaction, more readily than the primary alcohols. The higher alcohols of the series, $C_nH_{2n+2}O$, undergo this change when merely heated; cetyl alcohol, $C_{16}H_{34}O$, for example, is resolved by distillation into H_2O and cetene, $C_{16}H_{32}$.

3. By the decomposition of the paraffins, at the moment of their formation by the action of zinc or sodium on the alcoholic iodides of the monad alcohol-radicles, C_nH_{2n+1} (see p. 39).

4. By the action of the same iodides on the sodium-compounds of the same radicles; for example:

$$\underset{\substack{\text{Ethyl}\\\text{iodide.}}}{C_2H_5I} + \underset{\substack{\text{Sodium}\\\text{ethyl.}}}{C_2H_5Na} = \underset{\substack{\text{Sodium}\\\text{iodide.}}}{NaI} + \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Ethane.}}{C_2H_6}.$$

5. By decomposition of the hydroxides of ammonium bases containing four atoms of a monad alcohol-radicle (p. 25), these compounds when heated splitting up into a tertiary monamine (p. 24) and an olefine; thus:

$$\underset{\substack{\text{Tetrethylammon-}\\\text{ium hydroxide.}}}{N(C_2H_5)_4(HO)} = \underset{\substack{\text{Triethyl-}\\\text{amine.}}}{N(C_2H_5)_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Ethene.}}{C_2H_4}.$$

6. Olefines are formed by the decomposition of acetates and butyrates at a red heat, distilling over, together with several other products, from which they are separated by combining them with bromine, and heating the resulting bromine-compounds, $C_nH_{2n}Br_2$, to 275° with copper, water, and potassium iodide. In this manner Berthelot has obtained ethene, propene, butene, and pentene.

7. By electrolysis of the alkali-salts of bibasic acids; *e.g.*,

$$\underset{\text{Succinic acid.}}{C_4H_6O_4} = C_2H_4 + 2CO_2 + H_2.$$

8. By heating the diatomic haloïd ethers, $C_nH_{2n}Cl_2$, &c., with sodium:

$$C_2H_4Cl_2 + Na_2 = 2NaCl + C_2H_4.$$

9. Several of the olefines may be produced by direct synthesis from other hydrocarbons of simpler constitution, or their haloïd derivatives.

α. Ethene is formed by the action of nascent hydrogen upon ethine or acetylene:

$$C_2H_2 + H_2 = C_2H_4.$$

β. Propene, C_3H_6, is formed by passing a mixture of methane and carbon monoxide (oxymethene) through a red-hot tube:

$$2CH_4 + CO = H_2O + C_3H_6.$$

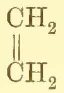
Also by the action of trichloromethane (chloroform) on zinc ethide:

$$2CHCl_3 + 3Zn(C_2H_5)_2 = 3ZnCl_2 + 4C_3H_6 + 2CH_4.$$

γ. Pentene, C_5H_{10}, or a compound isomeric or polymeric with it, is formed by the action of zinc ethide on propenyl (allyl) iodide:

$$2C_3H_5I + Zn(C_2H_5)_2 = ZnI_2 + 2C_5H_{10}.$$

Constitution and Reactions of the Olefines.—These hydrocarbons in the free state may be supposed to have one pair of their carbon-atoms linked together by two combining units; thus:



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$$

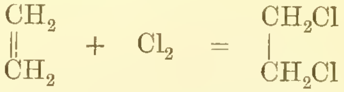
Ethene.

$$\begin{array}{c}CH_3\\ \|\\ CH\\ \|\\ CH_2\end{array}$$

Propene.

In all the higher members of the series this structure admits of isomeric modifications; three for butene, five for pentene, &c., as will presently be further considered.

With two carbon-atoms thus doubly linked, the olefines present the appearance of saturated molecules incapable of uniting with monatomic elements or radicles. Under the influence of chlorine, bromine, and iodine, however, they undergo a change of structure, the double linking of the two carbon-atoms being partly broken up, so that these atoms remain united by one combining unit only, and the hydrocarbon becomes a bivalent radicle, capable of taking up 2 atoms of chlorine, bromine, &c., thus:



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + Cl_2 = \begin{array}{c}CH_2Cl\\ |\\ CH_2Cl\end{array}$$

The resulting diatomic ethers, treated with silver acetate or potassium acetate, exchange their bromine for an equivalent quantity of the halogenic residue of the acetate, $C_2H_3O_2$ (p. 27), giving rise to diatomic acetic ethers; thus:

$$\underset{\text{Ethene bromide.}}{(C_2H_4)Br_2} + \underset{\text{Potassium acetate.}}{2C_2H_3O_2K} = \underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Ethene diacetate.}}{(C_2H_4)(C_2H_3O_2)_2};$$

and these ethers, distilled with a caustic alkali, yield diatomic alcohols or glycols; for example:

$$\underset{\text{Ethene diacetate.}}{(C_2H_4)(C_2H_3O_2)_2} + 2KHO = \underset{\text{Potassium acetate.}}{2C_2H_3O_2K} + \underset{\text{Ethene alcohol.}}{(C_2H_4)(OH)_2}.$$

5. The bromides, $C_nH_{2n}Br_2$, heated to 275° with a mixture of potassium iodide, copper, and water, give up their bromine and reproduce the original olefine, together with other hydrocarbons (p. 40).

6. Some olefines, when briskly shaken up with strong *sulphuric acid*, unite with it, forming acid ethers of sulphuric acid, which contain the monatomic alcohol-radicles analogous to the olefines; thus:

$$\underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethyl-sulphuric acid.}}{C_2H_5.HSO_4};$$

and these acid ethers distilled with water reproduce sulphuric acid and the monatomic alcohol analogous to the olefine:

$$\underset{\text{Ethyl-sulphuric acid.}}{C_2H_5.HSO_4} + \underset{\text{Water.}}{H(OH)} = H_2SO_4 + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)}.$$

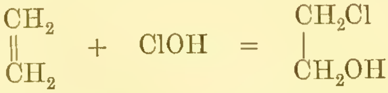
With fuming sulphuric acid (which contains sulphuric oxide in solution) the olefines yield sulpho-acids which are isomeric with the preceding, but are not decomposed by water with formation of an alcohol.

7. Olefines unite with *hydrochloric, hydrobromic, and hydriodic acids;* and the resulting compounds treated with silver oxide in presence of water, give rise to two different reactions which go on simultaneously, one part of the compound exchanging its halogen element for hydroxyl, and thereby producing an alcohol, while another portion gives up hydrochloric, hydrobromic, or hydriodic acid, reproducing the original olefine:

$$\underset{\substack{\text{Hexene}\\ \text{hydriodide.}}}{2(C_6H_{12}.HI)} + Ag_2O + H_2O = 2AgI + \underset{\substack{\text{Hexyl}\\ \text{alcohol.}}}{2C_6H_{14}O}$$

$$\underset{\text{Hexene hydriodide.}}{2(C_6H_{12}.HI)} + Ag_2O = 2AgI + H_2O + \underset{\text{Hexene.}}{2C_6H_{12}}$$

Olefines also unite with *hypochlorous acid,* forming compounds called glycolic chlorhydrins; *e.g.,*



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + ClOH = \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$$

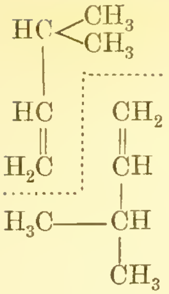
By *nascent hydrogen* (evolved by zinc and hydrochloric acid) they are converted into paraffins; *e.g.,* $C_2H_4 + H_2 = C_2H_6$.

They also yield paraffins when heated with concentrated *hydriodic acid,* the moniodoparaffin formed in the first instance being reduced by a second molecule of hydriodic acid; *e.g.,*

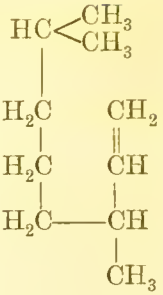
$$C_2H_4 + HI = C_2H_5I;\ \text{and}\ C_2H_5I + HI = C_2H_6 + I_2.$$

Condensation of the Olefines.—These bodies, under the influence of sulphuric acid, zinc chloride, boron fluoride, and other reagents, even at ordinary temperatures, become polymerised by the linking together of two or more molecules. In this manner isopentene or amylene, C_5H_{10}, may be converted into $C_{10}H_{20}$, $C_{15}H_{30}$, &c. Propene and butene may also be polymerised, but ethene is not polymerised either by sulphuric acid or by boron fluoride. The polymeric hydrocarbons thus formed are dyad radicles, capable of uniting directly with chlorine, &c.

The following diagram exhibits the conversion of isopentene or amylene into di-amylene, showing that the latter also has two of its carbon-atoms doubly linked, and may therefore act as a dyad radicle:



Amylene (2 mol.)



Diamylene.

Ethene, or **Ethylene,** C_2H_4, also called *Olefiant gas,* is produced in the dry distillation of many organic bodies, and is found, to the amount of about 6 per cent. in coal gas. It is most easily prepared by heating strong alcohol with three or four times its weight of strong sulphuric acid (i. 173). It is a colourless inflammable gas, which burns with a bright white flame. When exposed to a strong pressure at a temperature of $-110°$, it condenses to a liquid which does not solidify. Its specific gravity, referred to hydrogen as unity, is 14, showing that the molecule C_2H_4 has the normal 2-volume condensation:

$$\frac{2 \times 12 + 4 \times 1}{2} = 14.$$

Ethene unites readily with chlorine, bromine, and iodine, forming oily liquids. Fuming hydriodic acid absorbs it, with formation of ethyl iodide, C_2H_5I. It dissolves also in strong sulphuric acid, after prolonged agitation at ordinary temperatures, easily and completely at 160–175°. The product is ethylsulphuric acid, $C_2H_5.SO_4H$, which, when boiled with water, yields ethyl alcohol. Ethene is oxidised by chromic acid to aldehyde, C_2H_4O, and by potassium permanganate to oxalic and formic acid.

Propene, $C_3H_6 = CH_3—CH{=}CH_2$, is formed (1.) By heating propyl iodide or isopropyl iodide with alcoholic potash-solution:

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O\,;$$

(2.) By the action of nascent hydrogen (from zinc and hydrochloric acid), or of hydriodic acid, on allyl iodide:

$$C_3H_5I + HI = C_3H_6 + I_2\,;$$

(3.) Together with other products, by passing the vapour of ordinary amyl alcohol or butyl alcohol through a red-hot tube. It also occurs in coal gas.

Propene is a colourless gas, condensable to a liquid by strong pressure. It dissolves readily in strong hydriodic acid, forming secondary propyl iodide:

$$CH_2{-}CH{=}CH_2 + IH = CH_3{-}CHI{-}CH_3 .$$

Butene, or **Butylene**, C_4H_8. Of this hydrocarbon there are three modifications, represented by the following formulæ:

1. Butene,	$CH_3{-}CH_2{-}CH{=}CH_2$;
2. Pseudobutene,	$CH_3{-}CH{=}CH{-}CH_3$;
3. Isobutene,	$\begin{matrix}H_3C\\H_3C\end{matrix}{>}C{=}CH_2 .$

1. *Normal butene* is produced by abstraction of HI (action of alcoholic potash) from normal primary butyl iodide, $CH_3{-}CH_2{-}CH_2{-}CH_2I$, and by the action of zinc-ethide on bromethene:

$$2(CH_2{-}CHBr) + Zn{<}\begin{matrix}CH_2CH_3\\CH_2CH_3\end{matrix} = ZnBr_2 + 2(CH_3{-}CH_2{-}CH{=}CH_2).$$

It is gaseous at ordinary temperatures, and condenses at −10° to a liquid which boils at −5°. It unites with hydriodic acid, forming secondary butyl iodide, $CH_3{-}CH_2{-}CHI{-}CH_3$.

2. *Pseudobutene* is formed by heating secondary or pseudobutyl iodide, or the corresponding alcohol, with alcoholic potash, or with silver iodide. It boils at +3°, and solidifies at low temperatures. It unites with HI, reproducing secondary butyl iodide.

3. *Isobutene* is produced by the action of alcoholic potash on isobutyl iodide, $\begin{matrix}H_3C\\H_3C\end{matrix}{>}CH{-}CH_2I$, or on tertiary butyl iodide, $\begin{matrix}H_3C\\H_3C\end{matrix}{>}CI{-}CH_3$, or by that of sulphuric acid on the corresponding alcohols. It is also formed by passing the vapour of isopentyl alcohol through a red-hot tube, and by the electrolysis of isovaleric (ordinary valeric) acid.

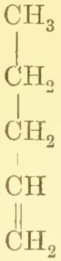
Isobutene is gaseous at ordinary temperatures, but condenses at very low temperatures to a liquid, which boils at −6°. Strong hydriodic acid absorbs it, with formation of tertiary butyl iodide. With sulphuric acid it forms, together with polymeric butenes, tertiary butylsulphuric acid, $\begin{matrix}H_3C\\H_3C\end{matrix}{>}C{<}\begin{matrix}CH_3\\SO_4H\end{matrix}$, which, when boiled with water, yields tertiary butyl alcohol.

The dibromides of the three isomeric butenes, $C_4H_8Br_2$, boil at the following temperatures:—

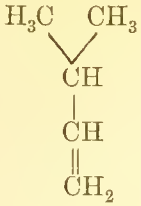
Normal.	Iso.	Pseudo.
166°	159°	149°

Pentenes, C_5H_{10}. Of the four possible modifications of these hydrocarbons, viz.,

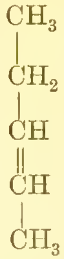
1.



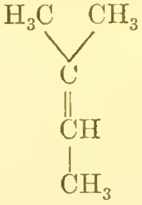
2.



3.



4.



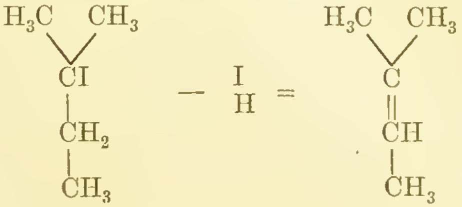
1. *Normal Pentene*, or *Ethyl-allyl*, $C_2H_5.C_3H_5$, is formed by the action of sodium on a mixture of the iodides of ethyl and allyl, or of zinc-ethyl on allyl iodide. It boils at 37°; unites with hydriodic acid to form the secondary iodide, $CH_3—CH_2—CH_2—CHI-CH_3$ or $IHC{<}\begin{smallmatrix}CH_3\\C_3H_7\end{smallmatrix}$. Its bromide, $C_5H_{10}Br_2$, boils at 175°.

2. *Isopentene*, or *Amylene*, is obtained, together with isopentane, by distilling ordinary amyl alcohol, $\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}{>}CH—CH_2—CH_2OH$, with sulphuric acid or zinc chloride. It is a colourless mobile liquid having a fragrant odour, a density of 0·663 at 0°, and boiling at 35°. Its bromide boils at 170–180°, with partial decomposition. Isopentene unites with hydriodic acid, forming another secondary pentyl iodide, $(CH_3)_2CH—CHI—CH_3$.

Isopentene shaken up with sulphuric acid (previously diluted with half its bulk of water, and cooled) is converted into several polymerides, viz., diamylene, $C_{10}H_{20}$, boiling at 156°; triamylene, $C_{15}H_{30}$, at 240–250°; tetramylene, $C_{20}H_{40}$, at 360°. They are oily liquids, uniting directly with bromine.

3. The third modification is not known with certainty, but is perhaps identical with a pentene, boiling at 25°, obtained by the action of concentrated alcoholic potash on isopentyl iodide.*

4. The fourth modification is obtained by the action of very strong alcoholic potash on tertiary pentyl iodide:



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* Flavitzky, Liebig's Annalen, clxix. 205.

It boils at 35°, unites with bromine, and with fuming hydriodic acid at 100°, reproducing the tertiary iodide.*

The higher olefines have been but little studied. They are obtained from the corresponding alcohols and iodides by the methods above described.

Hexene, or **Hexylene**, C_6H_{12}. Two hydrocarbons of this composition have been obtained, one from secondary, the other from tertiary hexyl alcohol. The former has a specific gravity of 0·699 at 0°, and boils at 65–66°; the latter, which occurs in the light oils from Boghead and Cannel tar, boils at 70°.

Heptene, or **Heptylene**, C_7H_{14}, also called *œnanthylene*, is formed from secondary heptyl chloride; also by treating heptyl aldehyde (œnanthol), $C_7H_{14}O$, with phosphorus pentachloride, and decomposing the resulting chloride, $C_7H_{14}Cl_2$, with sodium. It boils at 100°. The same hydrocarbon occurs in the light oils from Boghead and Cannel tar.

Octene, or **Octylene**, C_8H_{16}, occurs in the same oils, and is easily prepared by distilling secondary octyl alcohol with zinc chloride. It boils at 125°.

Cetene, $C_{16}H_{32}$, **Cerotene**, $C_{27}H_{54}$, and **Melene**, $C_{30}H_{60}$, are formed by destructive distillation of the corresponding alcohols, or substances containing them; cetene from spermaceti, cerotene from Chinese wax, melene from bees-wax.

Cetene is an oily liquid, boiling at 275°; cerotene, a crystalline solid; melene crystallises from hot alcohol in scales, which melt at 62°.

THIRD SERIES.—C_nH_{2n-2}.

Ethine or Acetylene Series.

These hydrocarbons may be arranged in two collateral series differing from one another in structure and in properties. The following are known :

α Series.			Boiling Point.	β Series.		Boiling Point.
Ethine	or Acetylene,	C_2H_2	...			
Propine	,, Allylene,	C_3H_4	...	β Allylene,	C_3H_4	...
				Crotonylene,	C_4H_6	18°
Pentine	,, α Valerylene,	C_5H_8	50°	β Valerylene,	C_5H_8	45°
Hexine	,, Hexoylene,	C_6H_{10}	80°	Diallyl,	C_6H_{10}	59°
Heptine,		C_7H_{12}	107°			
Octine,		C_8H_{14}	133°			
Decine,	,, Decenylene,	$C_{10}H_{18}$	165°	Rutylene,	$C_{10}H_{18}$	150°
Pentadecine	,, Benylene,	$C_{15}H_{28}$	225°			
Hexdecine	,, Cetenylene,	$C_{16}H_{30}$	280°			

A general method of preparing the hydrocarbons of the α-series, consists in heating the dibromides or di-iodides of the olefines with

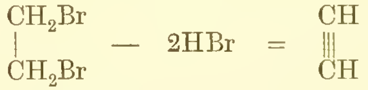
* Ermolaiew, Zeitschrift für Chemie, 1871, 275.

alcoholic potash, the reaction taking place by two stages, a monobrominated olefine being first formed, and then deprived by the further action of the potash, of the elements of hydrobromic acid; thus—

$$C_nH_{2n}Br_2 + KOH = KBr + H_2O + C_nH_{2n-1}Br,$$

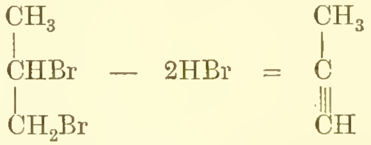
and $$C_nH_{2n-1}Br + KOH = KBr + H_2O + C_nH_{2n-2}.$$

The reaction amounts to the abstraction of 2HBr from the olefine dibromide, and shows that the hydrocarbons of this series have two of their carbon-atoms united by three combining units; thus:



$$\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array} \quad - \quad 2HBr \quad = \quad \begin{array}{c}CH\\ |||\\ CH\end{array}$$

Ethene dibromide. Acetylene.



$$\begin{array}{l}CH_3\\ |\\ CHBr\\ |\\ CH_2Br\end{array} \quad - \quad 2HBr \quad = \quad \begin{array}{l}CH_3\\ |\\ C\\ |||\\ CH\end{array}$$

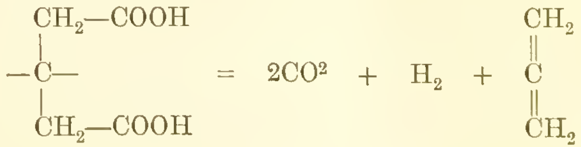
Propene dibromide. Allylene.

Acetylene does not admit of any other modification, at least in the free state; but in allylene, and the higher members of the series, another mode of grouping is possible, as shown by the following formulæ:

$$CH_2{=}C{=}CH_2 \qquad CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

β-Allylene. Diallyl.

The hydrocarbons of this latter (β) subseries are formed by various reactions, β-allylene, for example, by the electrolysis of itaconic acid:

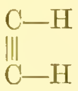


$$\begin{array}{c}CH_2{-}COOH\\ |\\ {-}C{-}\\ |\\ CH_2{-}COOH\end{array} \quad = \quad 2CO^2 \quad + \quad H_2 \quad + \quad \begin{array}{c}CH_2\\ \|\\ C\\ \|\\ CH_2\end{array}$$

Itaconic acid. β. Allylene.

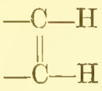
The hydrocarbons of the two subseries likewise differ in certain of their properties. Those of the α series, when treated with an ammoniacal solution of argentic or cuprous chloride, yield metallic derivatives, in the form of crystalline precipitates, which, when heated with hydrochloric acid, reproduce the original hydrocarbons. This reaction affords a convenient method of separating acetylene and allylene from other gases. The hydrocarbons of the β subseries do not yield these metallic derivatives.

When the hydrocarbons of the α subseries are subjected to the action of chlorine, bromine and other powerful reagents, the connection between the trebly-linked carbon-atoms becomes loosened,—as in the case of the olefines,—so that the molecule which was previously saturated becomes bivalent or quadrivalent: thus, in the case of acetylene,



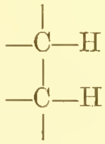
$$\begin{array}{l}\mathrm{C{-}H}\\ \,\,|||\\ \mathrm{C{-}H}\end{array}$$

Saturated.



$$\begin{array}{l}\mathrm{{-}C{-}H}\\ \quad\,||\\ \mathrm{{-}C{-}H}\end{array}$$

Bivalent.



$$\begin{array}{c}|\\ \mathrm{{-}C{-}H}\\ |\\ \mathrm{{-}C{-}H}\\ |\end{array}$$

Quadrivalent.

When agitated with hydrobromic or hydriodic acid, they take up one or two molecules of these acids. The dihydrobromides and dihydriodides thus produced have the same composition as the dibromides of the olefines; thus:

$$C_nH_{2n-2}.2HBr = C_nH_{2n}Br_2.$$

The two classes of bodies are, however, isomeric, not identical.

Acetylene, or **Ethine**, C_2H_2.—This hydrocarbon is one of the constituents of coal gas.—It is produced—1. By synthesis from its elements. When an electric arc from a powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, the carbon and hydrogen unite in the proportion to form ethine.

2. By the action of heat upon ethene, or the vapour of alcohol, ether, or wood-spirit, or by passing induction-sparks through marsh-gas.

3. By passing the vapour of chloroform over ignited copper:

$$2CHCl_3 + Cu_6 = 3Cu_2Cl_2 + C_2H_2.$$

4. By the incomplete combustion of bodies containing carbon and hydrogen; for example:

$$4CH_4 + O_6 = 6H_2O + 2C_2H_2$$
$$2C_2H_4 + O_2 = 2H_2O + 2C_2H_2.$$

It is produced in considerable quantity in the imperfect combustion which takes place in a Bunsen's gas-burner, when the flame strikes down and the gas burns at the small orifice at the bottom of the tube; it may be collected and purified by aspirating the gas through an ammoniacal copper or silver solution.

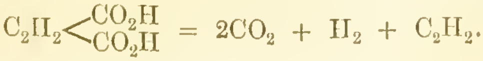
5. By passing a mixture of marsh-gas and carbon monoxide through a red-hot tube:

$$CH_4 + CO = H_2O + C_2H_2.$$

6. By the action of alcoholic potash on monobromethene:

$$C_2H_3Br + HKO = KBr + H_2O + C_2H_2.$$

7. By the electrolysis of fumaric or maleic acid

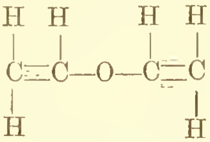


$$C_2H_2{<}\begin{array}{l}CO_2H\\ CO_2H\end{array} = 2CO_2 + H_2 + C_2H_2.$$

The crude acetylene obtained by either of these processes is purified in the manner above mentioned.

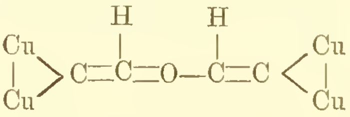
Acetylene is a colourless gas of specific gravity 0·92, having a peculiar and unpleasant odour, moderately soluble in water, not condensed by cold or pressure. It burns with a very bright and smoky flame, one volume of the gas consuming $2\frac{1}{2}$ volumes of oxygen and producing 2 volumes of carbon dioxide. When mixed with *chlorine,* it detonates almost instantly, even in diffused daylight, with separation of carbon.

Acetylene passed into an ammoniacal solution of *cuprous chloride* forms a red precipitate consisting of cuproso-vinyl oxide, $C_4(Cu_2)_2H_2O$, or $[C_2(Cu_2)H]_2O$, that is to say, vinyl-oxide $(C_2H_3)_2O$, having four of its hydrogen-atoms replaced by four atoms of (apparently) univalent copper (see i. 415). The constitution of this compound may be understood from the following formulæ:



$$\overset{H}{\underset{H}{C}}=\overset{H}{C}-O-\overset{H}{C}=\overset{H}{\underset{H}{C}}$$

Vinyl oxide.



$$\genfrac{}{}{0pt}{}{Cu}{Cu}{>}C=\overset{H}{C}=O-\overset{H}{C}=C{<}\genfrac{}{}{0pt}{}{Cu}{Cu}$$

Cuproso-vinyl oxide.

Its formation from cuprous chloride and acetylene is represented by the equation:

$$2Cu_2Cl_2 + 2C_2H_2 + H_2O = 4HCl + C_4Cu_4H_2O.$$

On heating it with hydrochloric acid, the opposite reaction takes place, cuprous chloride and water being reproduced, and pure acetylene evolved as gas.

When this copper compound is heated with zinc and dilute ammonia, the nascent hydrogen thereby evolved unites with the elements of ethine, producing ethene:

$$C_4Cu_4H_2O + 2H_2 = Cu_4 + H_2O + 2C_2H_2$$

and

$$C_2H_2 + H_2 = C_2H_4.$$

Acetylene, briskly agitated with strong *sulphuric acid,* is absorbed, producing vinyl-sulphuric acid, $C_2H_4SO_4$:

$$C_2H_2 + H_2SO_4 = (C_2H_3)HSO_4;$$

and this acid, distilled with water, is resolved into sulphuric acid and vinyl alcohol:

$$\underset{\text{Vinyl-sulphuric acid.}}{(C_2H_3)HSO_4} + H_2O = H_2SO_4 + \underset{\text{Vinyl alcohol.}}{C_2H_3(OH)}$$

Acetylene unites with *bromine,* forming a dibromide, $C_2H_2Br_2$.

When a series of strong induction sparks is passed through a mixture of acetylene and *nitrogen,* the two gases unite and form hydrocyanic acid: $C_2H_2 + N_2 = 2CNH$.

Bromacetylene, C_2HBr, is produced by the action of alcoholic potash on dibromethene dibromide :

$$C_2H_2Br_2.Br_2 = HBr + Br_2 + C_2HBr.$$

It is a spontaneously inflammable gas, which liquifies under a pressure of three atmospheres, is soluble in water, and very soluble in dibromethine. It unites with bromine, forming the compound $C_2HBr.Br_2$, and when passed into an ammoniacal solution of cuprous chloride, yields a precipitate of cuproso-vinyl oxide.

Allylene or **Propine**, C_3H_4.—This compound is produced by the action of sodium ethylate on bromopropene :

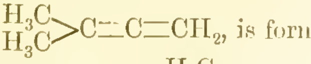
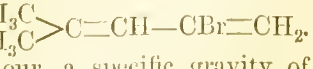
$$C_3H_5Br + C_2H_5NaO = NaBr + C_2H_5(HO) + C_3H_4,$$

its formation being a particular case of the general reaction given on page 59. It is a colourless gas, having an unpleasant odour, burning with a smoky flame, and forming, with mercurous salts, a grey precipitate ; with silver salts, a white precipitate ; and with cuprous chloride, a yellow precipitate, analogous in composition to that formed by ethine. With *bromine* it forms the compounds $C_3H_4Br_2$ and $C_3H_4Br_4$, the former boiling at 130°, the latter decomposing when distilled. With iodine it forms the compound $C_3H_4I_2$, which boils at 198°. It unites with 2 molecules of hydriodic acid, forming the compound $CH_3—CI_2—CH_3$, and similarly with HBr and HCl.

β Allylene, or *Allene*, $CH_2{=}C{=}CH_2$, is formed, as already stated, by the electrolysis of itaconic acid; also by the action of sodium on the modification of dichloropropene obtained from dichlorhydrin (see GLYCERIN) ; probably also from allyl iodide. With bromine it forms a crystalline tetrabromide, $C_3H_4Br_4$.

Crotonylene, C_4H_6 or $CH_3—CH{=}C{=}CH_2$, is formed by abstraction of BrH from monobromobutene, $CH_3—CH_2—CBr{=}CH_2$; also by distilling erythrite, $C_4H_{10}O_4$, with formic acid. It is a liquid boiling at 20°–25°, and forming a tetrabromide which crystallises in shining rhombic plates, melting at 116°. It does not form any metallic derivative with copper or silver, whence, and from its mode of formation, it may be referred to the β subseries.

Valerylene or **Pentine**, C_5H_8.—Of this hydrocarbon two modifications are known. *α Valerylene*, probably $HC{\equiv}C—C_3H_7$, is formed by abstraction of H_2Cl_2 from methylpropyl-ketonic chloride, $H_3C—CCl_2—C_3H_7$. It boils at 50°, and yields metallic derivatives with silver and copper.

β Valerylene, probably  $\begin{matrix}H_3C\\H_3C\end{matrix}\!>C{=}C{=}CH_2$, is formed by abstraction of HBr from bromisopentene,  $\begin{matrix}H_3C\\H_3C\end{matrix}\!>C{=}CH—CBr{=}CH_2$. It is a liquid having an alliaceous odour, a specific gravity of 0·700, and boiling at 45°. It does not form compounds with silver and copper. It forms a dibromide which boils at 170°, and a liquid tetrabromide.

Hexines, C_6H_{10}.—*Hexoylene*, probably $CH_3—(CH_2)_3—C{\equiv}CH$, obtained by abstraction of HBr from monobromhexene, boils at 76–80°.

Diallyl, $H_2C{=}CH—CH_2—CH_2—CH{=}CH_2$, is formed by the action of sodium or silver on allyl iodide. It is a volatile, pungent liquid, boiling at 59°, and forming a crystalline tetrabromide and tetriodide, the former melting at 63°. When shaken with aqueous hypochlorous acid, it forms the compound $C_6H_{10}Cl_2(OH)_2$. Heated with concentrated hydriodic acid it yields the compound $C_6H_{12}I_2$ or $H_3C—CHI—CH_2—CH_2—CHI—CH_3$, as a heavy oily liquid; and on heating this compound with silver acetate, it is converted into the corresponding diacetate, which, when heated with caustic potash, yields the corresponding hexene glycol,

$$H_3C—CHOH—CH_2—CH_2—CHOH—CH_3.$$

The higher members of the series C_nH_{2n-2} are obtained either from the dibromides of the corresponding olefines, or from substitution-products isomeric therewith. Thus heptine, or œnanthidene, is formed by the action of potash on œnanthidene dibromide (obtained by treating œnanthyl with phosphorus pentachloride); rutylene is prepared from diamylene; and the isomeric body decine or decenylene from the dibrominated derivative of the hydrocarbon $C_{10}H_{22}$, which exists in petroleum.

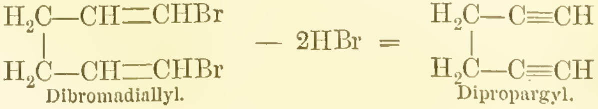
SERIES C_nH_{2n-4}.

The only known members of the fatty group belonging to this series is valylene or pentone, C_5H_6, which is formed by the action of alcoholic potash on valerylene dibromide, $C_5H_8Br_2$. It is a light oil, smelling like garlic, and boiling at about 50°. It forms precipitates with ammoniacal copper and silver solutions. With bromine in a freezing mixture, it yields a crystalline mass consisting of $C_5H_6Br_6$, saturated with a thick liquid which is a mixture of the same compound with $C_5H_6Br_4$, and probably $C_5H_6Br_2$.

The terpenes, $C_{10}H_{16}$, also come under the formula C_nH_{2n-4}, but they belong rather to the aromatic group.

SERIES C_nH_{2n-6}.

Dipropargyl, C_6H_6 or $HC{\equiv}C—CH_2—CH_2—C{\equiv}CH$, the only known hydrocarbon of the fatty group belonging to this series, is isomeric with benzene, but differs greatly from that body in its properties. It is prepared by distilling diallyl tetrabromide, $C_6H_{10}Br_4$, with a large excess of caustic potash, whereby it is converted into dibromodiallyl, $C_6H_8Br_2$, and boiling the latter with alcoholic potash:



$$\begin{array}{lcl} H_2C—CH{=}CHBr & & H_2C—C{\equiv}CH \\ \quad| & -\ 2HBr\ = & \quad| \\ H_2C—CH{=}CHBr & & H_2C—C{\equiv}CH \end{array}$$

Dibromadiallyl. Dipropargyl.

Dipropargyl is a mobile, limpid, highly refractive liquid, having an intensely pungent odour, a specific gravity of 0·81 at 18°, and boiling at 85°. With ammoniacal cuprous chloride it forms a greenish-yellow precipitate, $C_6H_4Cu_2 + 2H_2O$, and with silver nitrate, a white precipitate, $C_6H_4Ag_2 + 2H_2O$, which blackens on exposure to light, and explodes at 100°, leaving carbon and silver.

Dipropargyl is easily distinguished from benzene by its property of combining explosively with bromine, forming the tetrabromide $C_6H_6Br_4$, a viscid liquid, of specific gravity 2·460 at 19°, which combines in the dark with more bromine, forming the octobromide $C_6H_6Br_8$, which boils at 140°.

HALOGEN DERIVATIVES OF THE HYDROCARBONS.

HALOÏD ETHERS.

These compounds are formed, as already observed, by substitution of a halogen element (Br,Cl,I) for an equivalent quantity of hydrogen in a hydrocarbon, or of hydroxyl in the corresponding alcohol. They are monatomic, diatomic, triatomic, &c., according as 1, 2, 3, or more atoms of the halogen are thus introduced.

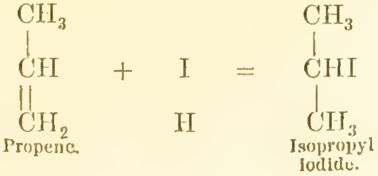
Monatomic Haloïd Ethers, $C_nH_{2n+1}X$.—These ethers are derived from the paraffins. Chlorine and bromine act directly on these hydrocarbons, the action of the former being accelerated by light, that of the latter by heat. Iodine likewise acts on the paraffins, removing an atom of hydrogen, and taking its place; but the iodoparaffin thus formed is for the most part reconverted into the original hydrocarbon by the action of the hydriodic acid formed at the same time: thus,

$$C_3H_7I + HI = C_3H_8 + I_2$$

This reverse action may, however, be prevented by the addition of a substance, like mercuric oxide, which decomposes the hydriodic acid as fast as it is formed, and in that case an iodoparaffin or alcoholic iodide is obtained: *e.g.*,

$$2C_3H_8 + 2I_2 + HgO = 2C_3H_7I + H_2O + HgI_2.$$

These monatomic haloïd ethers are also produced by the action of the haloïd compounds of hydrogen and of phosphorus on the corresponding alcohols (*q.v.*), and by addition of a haloïd acid to an unsaturated hydrocarbon, *i.e.*, a hydrocarbon in which a pair of carbon-atoms are joined together by two combining units (p. 54): *e.g.*,



$$\begin{array}{ccccc} CH_3 & & & & CH_3 \\ | & & & & | \\ CH & + & I & = & CHI \\ \| & & & & | \\ CH_2 & & H & & CH_3 \\ \text{Propene.} & & & & \text{Isopropyl iodide.} \end{array}$$

These ethers are converted—

α. Into the original **paraffins** by the action of *nascent hydrogen* (evolved by hydrochloric acid and zinc, or by sodium amalgam):

β. Into the corresponding **alcohols** by the action of moist *silver oxide:*

$$C_2H_5I + AgOH = AgI + C_2H_5OH.$$

Potassium hydroxide acts in a similar manner, but the resulting alcohol (especially if a secondary alcohol) is partly converted by dehydration into the corresponding olefine, *e.g.*, $C_3H_8O - H_2O = C_3H_6$.

γ. Into **oxygen-ethers** by the action of the sodium or potassium derivatives of the alcohols; thus,

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + \underset{\text{Sodium ethylate.}}{NaOC_2H_5} = NaI + \underset{\text{Ethyl oxide.}}{C_2H_5.O.C_2H_5}$$

δ. Into **compound ethers** by the silver salts of the corresponding acids;

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + \underset{\text{Silver acetate.}}{AgC_2H_3O_2} = AgI + \underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2}$$

The individual ethers of this group will be described in connection with the corresponding alcohols.

Monatomic Haloïd Ethers, $C_nH_{2n-1}X$.

These ethers are derived from the olefines, C_nH_{2n}, by substitution of 1 atom of chlorine, &c., for hydrogen. They cannot, however, be formed by direct substitution, as the action of chlorine, bromine, or iodine on the olefines gives rise to addition-products, $C_nH_{2n}Cl_2$, &c.; but they may be obtained by treating these addition-products with alcoholic potash or silver oxide; thus,

$$C_2H_4Cl_2 + KOH = KCl + H_2O + C_2H_3Cl.$$

These ethers, like the olefines from which they are derived, can take up 2 atoms of chlorine, bromine, or iodine, forming compounds which can likewise give up hydrochloric, hydrobromic, or hydriodic acid, under the influence of alcoholic potash; the body thus formed can again take up 2 atoms of chlorine, bromine, or iodine, then give up HCl, HBr, or HI; and thus, by a series of perfectly similar reactions, we at length arrive at bodies consisting of the primitive olefine with all its hydrogen replaced by chlorine, bromine, or iodine, and the dichlorides, dibromides, and di-iodides of these last-mentioned bodies: thus, from ethene may be derived the following series of brominated compounds:

Ethene, ...	C_2H_4	Ethene bromide, . . .	$C_2H_4Br_2$
Bromethene, . .	C_2H_3Br	Bromethene bromide, .	$C_2H_3Br \,.\, Br_2$
Dibromethene, . .	$C_2H_2Br_2$	Dibromethene bromide, .	$C_2H_2Br_2 .\, Br_2$
Tribromethene, . .	C_2HBr_3	Tribromethene bromide,	$C_2HBr_3 \,.\, Br_2$
Tetrabromethene, .	C_2Br_4	Tetrabromethene bromide,	$C_2Br_4 \,.\, Br_2$

Further, a monochlorinated or monobrominated olefine may give up the atom of chlorine or bromine which it contains, in the form of hydrochloric or hydrobromic acid, whereby it is reduced to a hydrocarbon of the series, C_nH_{2n-2}. This reaction may take place at 130°–150°, under the influence of alcoholic potash, or, better, of sodium ethylate (obtained by dissolving sodium in anhydrous alcohol); thus:

$$\underset{\text{Bromethene.}}{C_2H_3Br} + \underset{\substack{\text{Sodium}\\\text{ethylate.}}}{NaOC_2H_5} = NaBr + \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} + \underset{\text{Acetylene.}}{C_2H_2}$$

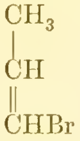
Chlorethene or *Vinyl Chloride*, $C_2H_3Cl = CH_2{=}CHCl$ (the univalent radicle $CH_2{=}CH—$ being called *vinyl*), is a gas having an alliaceous odour, and liquefying at 18°.

Bromethene or *Vinyl Bromide*, C_2H_3Br, smells like the chloride, has a specific gravity of 1·52, and boils at 23°. When kept in sealed tubes, it sometimes solidifies to a white amorphous mass, having the appearance of porcelain.

Iodethene or *Vinyl iodide*, C_2H_3I, has a specific gravity of 1·98, and boils at 55°.

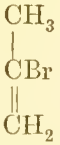
Propene yields three series of monatomic haloïd ethers: *e.g.*,

(1.)



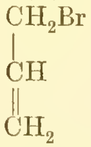
$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CHBr \end{array}$$

(2.)



$$\begin{array}{l} CH_3 \\ | \\ CBr \\ \| \\ CH_2 \end{array}$$

(3.)



$$\begin{array}{l} CH_2Br \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

1. The only known ether of the first group is the bromide, which is a liquid boiling at 48°, produced by addition of hydrobromic acid to allylene:

$$CH_3—C{\equiv}CH + HBr = CH_3—CH{=}CHBr.$$

2. The ethers of the second group, called chloropropene, &c., are formed by the action of alcoholic potash on the chloride &c., of propene, the action consisting in the abstraction of HCl, &c. (p. 66):

$$CH_3—CHCl—CH_2Cl - HCl = CH_3—CCl{=}CH_2;$$

also from acetone chloride (p. 71):

$$CH_3—CCl_2—CH_3 - HCl = CH_3—CCl{=}CH_2.$$

Chloropropene has a specific gravity of 0·918 at 9°, and boils at 23°. *Bromopropene* has a specific gravity of 1·411 at 15°, and boils at 57·6°.

It unites directly with hydrogen bromide, forming propene bromide $CH_3—CHBr—CH_2Br$, and acetone bromide, $CH_3—CBr_2—CH_3$.

3. The ethers of the third group, called allyl ethers, are analogous in constitution to allyl alcohol, $CH_2OH—CH{=}CH_2$, and will be described in connection therewith.

Diatomic Haloïd Ethers, $C_nH_{2n}X_2$.

These ethers are formed: 1. From the paraffins, by direct substitution of Cl_2, Br_2, &c.; for H_2. 2. From the olefines, C_nH_{2n}, by direct addition of Cl_2, &c. 3. By the action of the chlorides, bromides, and iodides of phosphorus on aldehydes and ketones; thus,

$$\underset{\text{Aldehyde.}}{C_2H_4O} + PCl_5 = \underset{\text{Dichlorethane.}}{C_2H_4Cl_2} + POCl_3$$

$$\underset{\text{Acetone.}}{C_3H_6O} + PCl_5 = \underset{\text{Dichloropropane.}}{C_3H_6Cl_2} + POCl_3$$

Methane Derivatives.—*Dichloromethane*, CH_2Cl_2, is formed by chlorination of methyl chloride, CH_3Cl; and by the action of chlorine on di-iodomethane or on methyl iodide:

$$CH_3I + Cl_2 = CH_2Cl_2 + HI.$$

It is a colourless liquid, having a specific gravity of 1·36 at 0°, and boiling at 40°.

Di-iodomethane, CH_2I_2, is produced by heating trichloro- or tri-iodomethane to 130° with fuming hydriodic acid:

$$CHCl_3 + 4HI = CH_2I_2 + I_2 + 3HCl.$$

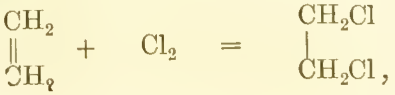
It crystallises in colourless shining laminæ of specific gravity 3·34 at 0°, melts at 6°, and boils at 182°.

Ethane Derivatives, $C_2H_4X_2$.—These ethers admit of two modifications, accordingly as the two atoms of the chlorous radicle X are attached to different atoms, or to the same atom of carbon; thus,

$$\begin{array}{l} CH_2X \\ | \\ CH_2X \end{array}$$

$$\begin{array}{l} CH_3 \\ | \\ CHX_2 . \end{array}$$

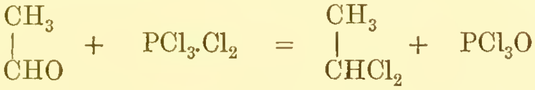
The ethers of the first modification are formed by direct addition of chlorine, bromine, or iodide, to ethene; the double linking of the two carbon-atoms in the molecule of free ethene being loosened by the entrance of the two chlorine-atoms into the group, and the ethene then becoming a bivalent radicle; thus,



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + Cl_2 = \begin{array}{l} CH_2Cl \\ | \\ CH_2Cl , \end{array}$$

These ethers are accordingly regarded as chloride, bromide, or iodide, of ethene.

The ethers of the second modification are produced by the action of the perchloride, &c., of phosphorus on aldehyde, the reaction consisting in the replacement of the oxygen-atom of this compound by 2 atoms of chlorine, &c., *e.g.*,

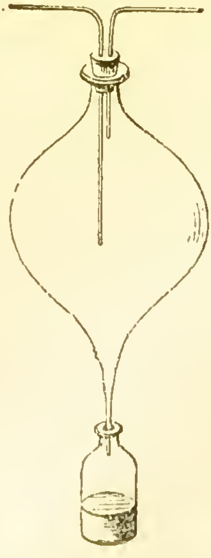


$$\begin{matrix}CH_3\\ |\\ CHO\end{matrix} + PCl_3.Cl_2 = \begin{matrix}CH_3\\ |\\ CHCl_2\end{matrix} + PCl_3O$$

They may be supposed to contain the bivalent radicle ethidene, $CH_3{-}CH{=}$; but this radicle has not been isolated.

Ethene Chloride, $\begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix}$.—This compound has long been known by the name of *Dutch liquid*, having been discovered by four Dutch chemists in 1795. When equal measures of ethene gas and chlorine are mixed over water, absorption of the mixture takes place, and a yellowish oily liquid is produced, which collects upon the surface of the water, and ultimately sinks to the bottom in drops. It may be easily prepared, in quantity, by causing the two gases to combine in a glass globe (fig. 13) having a narrow neck at the lower part, dipping into a small bottle, to receive the product. The two gases are conveyed by separate tubes, and allowed to mix in the globe, the ethene gas being kept a little in excess. The chlorine should be washed with water, and the ethene passed through strong oil of vitriol, to remove vapour of ether: the presence of sulphurous and carbonic acids is not injurious. Combination takes place very rapidly, and the liquid product trickles down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated, first with water, and afterwards with concentrated sulphuric acid, and, lastly, purified by distillation.

Fig. 13.



Pure ethene chloride is a thin, colourless liquid, of fragrant odour and sweet taste: it is slightly soluble in water, and readily so in alcohol and ether. It has a specific gravity 1·271 at 0°, and boils at 85°. It is unaffected by oil of vitriol or solid potassium hydrate. When inflamed it burns with a greenish, smoky light. When treated with an alcoholic solution of potash, it is slowly resolved into potassium chloride, which separates, and chlorethene, C_2H_3Cl, whose vapour requires to be cooled down to −18° before it condenses; at this temperature it forms a limpid, colourless liquid. Chlorine is absorbed by this latter substance, and a compound is produced, which contains $C_2H_3Cl_3$; and this is in turn decomposed by an alcoholic solution of potash into potassium chloride and another volatile liquid, $C_2H_2Cl_2$. This series of reactions is analogous to that already noticed in the case of the bromine compounds (p. 67).

Ethidene Chloride, $CH_3—CHCl_2$, is best prepared by the action of phosphoric chloride on aldehyde: it is also formed by the action of chlorine on ethyl chloride. It is a colourless liquid smelling like chloroform, having a specific gravity of 1·198, and boiling at 58°–59°. When subjected to the action of chlorine, it yields the compounds $CH_3.CCl_3$ and $CH_2Cl.CHCl_2$, together with other products.

Ethene Bromide, $CH_2Br—CH_2Br$, obtained by saturating bromine with olefiant gas, is an oily fragrant liquid, of specific gravity 2·163 at 21°, boiling at 129°, and solidifying at 0° to a crystalline mass which melts at 9°.

Ethidene Bromide, $CH_3—CHBr_2$, obtained similarly to the chloride, is a liquid boiling at 110–114°, and decomposing when heated with water.

These two bromides are also formed by heating monobromethene, $CH_2{=}CHBr$, with hydrobromic acid, the ethene compound when the acid is highly concentrated, the ethidene compound when it is more dilute.

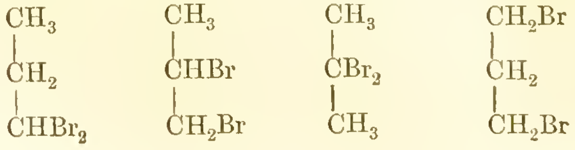
Ethene Iodide, $CH_2I—CH_2I$, is produced by the direct combination of iodine with ethene in sunshine or under the influence of heat, also by passing ethene gas into an alcoholic solution of iodine. It crystallises from alcohol in shining needles, melts at 73°, and decomposes at higher temperatures into ethene and iodine.

Ethidene Iodide, $CH_3I—CHI_2$, is obtained by heating the chloride with aluminium iodide:

$$3C_2H_4Cl_2 + 2AlI_3 = 2AlCl_3 + 3C_2H_4I_2;$$

also by addition of hydriodic acid to acetylene: $C_2H_2 + 2HI = C_2H_4I_2$. It is a liquid having a specific gravity of 2·84 at 0°, and boiling at 178°.

Propane Derivatives, $C_3H_6X_2$.—The diatomic ethers derived from propane admit of four modifications, as exhibited by the following formulæ of the bromide:



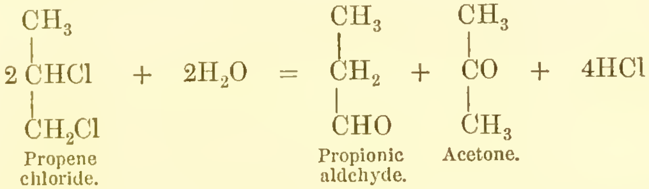
1. Propidene bromide.	2. Propene bromide.	3. Methylbromacetol.	4. Trimethene bromide.
$\begin{array}{l}CH_3\\ \vert\\ CH_2\\ \vert\\ CHBr_2\end{array}$	$\begin{array}{l}CH_3\\ \vert\\ CHBr\\ \vert\\ CH_2Br\end{array}$	$\begin{array}{l}CH_3\\ \vert\\ CBr_2\\ \vert\\ CH_3\end{array}$	$\begin{array}{l}CH_2Br\\ \vert\\ CH_2\\ \vert\\ CH_2Br\end{array}$

1. The propidene or propylidene ethers are formed by the action of phosphorus pentachloride, &c., on propylic aldehyde, $CH_3—CH_2—CHO$. The *chloride* is a liquid having an alliaceous odour, and boiling at 84–87°. The bromide and iodide are not known.

2. The propene or propylene ethers are formed by direct combination of propene with chlorine, bromine, and iodine. When treated with silver oxide and water they are converted into propene alcohol or propylene glycol, $CH_3—CHOH—CH_2OH$.

The *chloride*, $CH_3—CHCl—CH_2Cl$, is also formed by the action of chlorine, in sunshine and in presence of iodine, on pseudopropyl chloride, $CH_3—CHCl—CH_3$. If iodine is not present, acetone chloride is formed at the same time. Propene chloride has a specific gravity of 1·165 at 14°, and boils at 98°. The *bromide*, formed by direct combination or by the action of bromine on pseudopropyl bromide, is a liquid of specific gravity 1·946 at 17°, and boiling at 142°. The *iodide*, produced by direct combination of propene with iodine at 50°, is a colourless oil not distillable without decomposition.

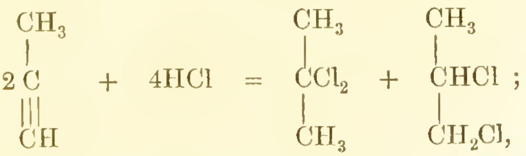
The chloride or bromide of propene heated with water to 200° is converted into propionic aldehyde and acetone:



$$2\begin{array}{c}CH_3\\|\\CHCl\\|\\CH_2Cl\end{array} + 2H_2O = \begin{array}{c}CH_3\\|\\CH_2\\|\\CHO\end{array} + \begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + 4HCl$$

3. The propene derivatives of the form, $CH_3—CX_2—CH_3$, are produced from acetone by substitution of Cl_2 or Br_2 for O, the substitution being effected by the action of PCl_5 or PBr_5.

Acetone chloride or *Methylchloracetol*, $CH_3—CCl_2—CH_3$, is also produced, together with propene chloride, by addition of HCl to allylene, C_3H_4, thus:



$$2\begin{array}{c}CH_3\\|\\C\\|||\\CH\end{array} + 4HCl = \begin{array}{c}CH_3\\|\\CCl_2\\|\\CH_3\end{array} + \begin{array}{c}CH_3\\|\\CHCl\\|\\CH_2Cl,\end{array};$$

and by chlorination of pseudopropyl chloride. It is a colourless liquid of specific gravity 1·827 at 16°, and boiling at 70°. Sodium reduces it to ordinary propene. With alcoholic potash it gives chloropropene, $CH_3—CCl{=}CH_2$, which is also formed in the same manner from propene dichloride. Heated to 150° with water, it is partially converted into acetone.

4. **Trimethene Bromide**, $CH_2Br—CH_2—CH_2Br$, is formed by heating allyl alcohol, $CH_2═CH—CH_2OH$, with hydrobromic acid; also, together with propene bromide, by heating allyl bromide to 100° with hydrobromic acid. It is a colourless liquid, of specific gravity 1·93 at 19°, and boiling at 162°; converted by alcoholic potash into allyl bromide and allyl-ethyl oxide, $CH_2═CH—CH_3—O—C_2H_5$.

Trimethene chloride, $CH_2Cl—CH_2—CH_2Cl$, formed by heating the bromide to 169° with mercuric chloride, is a fragrant liquid, having a specific gravity of 1·201 at 15°, boiling at 117°; converted by alcoholic potash into allyl-ethyl oxide.

Triatomic Haloïd Ethers, $C_nH_{2n-1}X_3$.

Methenyl Chloride, or **Chloroform**, $CHCl_3$.—This compound is produced :—1. Together with methene chloride, CH_2Cl_2, when a mixture of chlorine and gaseous methyl chloride is exposed to the sun's rays. 2. By the action of alkalis on chloral (trichloraldehyde):

$$\underset{\text{Chloral.}}{C_2HCl_3O} + KOH = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Potassium formate.}}{CHKO_2}$$

3. By boiling trichloracetic acid with aqueous alkalis :

$$C_2HCl_3O_2 + 2KOH = CHCl_3 + K_2CO_3 + H_2O\,.$$

4. By the action of nascent hydrogen on carbon tetrachloride:

$$CCl_4 + H_2 = HCl + CHCl_3.$$

5. By the action of hypochlorites, or of chlorine in presence of alkalis, on various organic substances, as methyl-, ethyl-, and amyl-alcohols, acetic acid, acetone, &c. The reaction is complicated, giving rise to several other products ; with common alcohol and calcium hypochlorite the principal reaction appears to be—

$$2C_2H_6O + 5CaCl_2O_2 = 2CHCl_3 + 2CaCO_3 + 2CaCl_2 + CaH_2O_2 + 4H_2O\,.$$

Chloroform is prepared on the large scale by cautiously distilling together good commercial chloride of lime, water, and alcohol. The whole product distils over with the first portions of water, so that the operation may be soon interrupted with advantage. The chloroform, which constitutes the oily portion of the distillate, is purified by agitation with water, desiccation with calcium chloride, and distillation in a water-bath.

Chloroform is a thin colourless liquid of agreeable ethereal odour, much resembling that of Dutch liquid, and of a sweetish taste. Its density is 1·525 at 0°, and it boils at 61°: the density of its vapour (compared with air) is 4·20. Chloroform is difficult to kindle, and burns with a greenish flame. It is nearly insoluble in water, and is not affected by concentrated sulphuric acid. When boiled with aqueous potash in a closed tube, it is converted into potassium chloride and formate:

$$CHCl_3 + 4HOK = 3KCl + CHKO_2 + 2H_2O.$$

Chloroform is well known for its remarkable effects upon the animal system, in producing temporary insensibility to pain when its vapour is inhaled.

Bromoform, $CHBr_3$, is a heavy, volatile liquid, prepared by the simultaneous action of bromine and aqueous alkalis on alcohol, wood-spirit, and acetone. It has a density of 2·9 at 12°, solidifies at −9°, and boils at 150–152°. It is converted by caustic potash into potassium bromide and formate.

Iodoform, CHI_3, is a solid, yellow, crystallisable substance, easily obtained by adding alcoholic solution of potash to tincture of iodine, avoiding excess, evaporating the whole to dryness, and treating the residue with water. It melts at 119°, and distils with vapour of water. It is nearly insoluble in water, but dissolves in alcohol, and is decomposed by alkalis in the same manner as the preceding compounds. Bromine converts it into bromiodoform, $CHBr_2I$, a colourless liquid which solidifies at 0°. Iodoform distilled with phosphorus pentachloride or mercuric chloride, is converted into chloriodoform, $CHCl_2I$, a colourless liquid of specific gravity 1·96, which does not solidify at any temperature.

Trichlorethane, $C_2H_3Cl_3$, admits of two modifications, viz.: (1.) $CH_3—CCl_3$, formed by the action of chlorine in sunshine on ethyl chloride. It is a liquid smelling like chloroform, boiling at 74·5°, and converted by alcoholic potash into acetic acid:

$$CH_3.CCl_3 + 4KOH = CH_3.CO.OK + 3KCl + 2H_2O.$$

(2.) $CH_2Cl—CHCl_2$, obtained by the action of chlorine on vinyl chloride, $H_2C{=}CHCl$ (see VINYL ALCOHOL). It boils at 115°, and has a specific gravity of 1·422 at 0°. Alcoholic potash-solution converts it into dichlorethene, $C_2H_2Cl_2$.

Tribromethane, $C_2H_3Br_3$, is obtained by adding bromine to bromethene, C_2H_3Br, cooled by a freezing mixture. It is a colourless liquid, which smells like chloroform, has a specific gravity of 2·620 at 23°, and boils at 186·5°. Alcoholic potash abstracts HBr, converting it into dibromethene, $C_2H_2Br_2$.

Trichloropropane, $C_3H_5Cl_3$, admits of four modifications, represented by the following formulæ:

(1.) $CH_3—CH_2—CCl_3$. (3.) $CH_3—CCl_2—CH_2Cl$.
(2.) $CH_3—CHCl—CHCl_2$. (4.) $CH_2Cl—CHCl—CH_2Cl$.

The last of these, which is the most important, is analogous in composition to glycerin, $C_3H_5(OH)_3$, and will be described, together with the corresponding bromine- and iodine-derivatives, in connection with that compound.

Haloïd Ethers of Higher Orders.

Tetrachloromethane, or **Carbon Tetrachloride,** CCl_4, is formed by passing the vapour of carbon bisulphide, together with chlorine, through a red-hot porcelain tube. A mixture of sulphur chloride and carbon tetrachloride is formed, which is distilled with potash, whereby the chloride of sulphur is decomposed, and pure carbon tetrachloride passes over. It is a colourless liquid of 1·56 specific gravity, and boils at 77°. The same compound is formed by exhausting the action of chlorine upon marsh-gas or methyl chloride in sunshine. An alcoholic solution of potash converts it into a mixture of potassium chloride and carbonate.

Tetrabromomethane, or **Carbon Tetrabromide,** CBr_4, is formed by the action of bromine, in presence of iodine bromide or antimonious bromide, on carbon sulphide, bromopicrin, bromoform, or chloroform. It is a white crystalline substance, having a specific gravity of 3·42 at 14°, melts at 91°, and boils with slight decomposition at 189·5°. Heated to 100° with alcohol in a sealed tube, it yields hydrogen bromide, aldehyde, and bromoform :

$$CBr_4 + C_2H_6O = HBr + C_2H_4O + CHBr_3.$$

Tetra-iodomethane, or **Carbon Tetra-iodide,** CI_4, is produced by heating tetrachlorethane with iodide of aluminium. It crystallises from ether in dark-red regular octohedrons of specific gravity 4·32 at 20°, and decomposes on exposure to the air, especially at high temperatures, yielding iodine and carbon dioxide.

Tetrabromethane, $C_2H_2Br_4$, formed by direct combination of bromine with dibromethene, $C_2H_2Br_2$, or with acetylene, C_2H_2, is a liquid having a specific gravity of 2·88 at 22°, boiling at 200°, and solidifying in a freezing mixture to a white crystalline mass. By heating with alcoholic potash it is converted into tribromethene, $CHBr_3$.

Tetrabromethene, or **Carbon Dibromide,** C_2Br_4, is formed by the action of alcoholic potash on pentabromethane :

$$C_2HBr_5 + KOH = C_2Br_4 + KBr + H_2O,$$

or by treating common alcohol or ether with bromine :

$$\underset{\text{Alcohol.}}{C_2H_6O} + 8Br = C_2Br_4 + 4HBr + H_2O$$

$$\underset{\text{Ether.}}{C_4H_{10}O} + 16Br = 2C_2Br_4 + 8HBr + H_2O.$$

It crystallises in white plates, melts at 50°, and sublimes without alteration.

Tetrachlorethene, or **Carbon Dichloride**, C_2Cl_4, obtained by passing the vapour of the trichloride or tetrachloride through a red-hot tube, either alone or mixed with hydrogen, or by the action of nascent hydrogen (zinc and dilute sulphuric acid) on the trichloride, is a mobile liquid of specific gravity 1·629, boiling at 117°. When heated to 200° with potassium hydroxide, it is completely converted into potassium chloride and oxalate, with evolution of hydrogen :

$$C_2Cl_4 + 6KOH = 4KCl + C_2K_2O_4 + 2H_2O + H_2.$$

It absorbs chlorine and bromine in sunshine, forming in the one case the trichloride, C_2Cl_6, and in the other the chlorobromide, $C_2Cl_4Br_2$.

Pentabromethane, C_2HBr_5, obtained by slowly distilling tribromethene, C_2HBr_3, with bromine, or by the action of bromine on acetylene, crystallises from alcohol in prisms smelling like camphor, melting at 45–50°, and decomposed by distillation.

Hexbromethane, or **Carbon Tribromide**, C_2Br_6, is formed by heating the dibromide with bromine in a sealed tube, or by heating either of the compounds, $C_2H_2Br_4$, C_2HBr_5, with bromine in a sealed tube :

$$C_2H_2Br_4 + Br_4 = 2HBr + C_2Br_6$$
$$C_2HBr_5 + Br_2 = HBr + C_2Br_6.$$

This compound dissolves sparingly in alcohol or ether, easily in carbon sulphide, from which it separates on evaporation in hard rather thick rectangular prisms. At 200°–210° it melts and decomposes, yielding carbon dibromide and free bromine.

Hexchlorethane, or **Carbon Trichloride**, $C_2Cl_6 = CCl_3—CCl_3$, is the final product of the action of chlorine in sunshine on ethyl chloride, C_2H_5Cl, or ethene chloride, $C_2H_4Cl_2$. It is a white, crystalline substance, of aromatic odour, insoluble in water, but easily dissolved by alcohol and ether : it melts at 160°, and boils at 182°. It burns with difficulty, and is not altered by distillation with aqueous or alcoholic potash. Its vapour, passed through a red-hot porcelain tube filled with fragments of glass or rock-crystal, is decomposed into free chlorine, and the dichloride, C_2Cl_4.

Tetrachlorodibromethane, or **Carbon Chlorobromide**, $C_2Cl_4Br_2$, formed by the action of bromine in sunshine on the dichloride, C_2Cl_4, is a white crystalline body resembling the trichloride.

Carbon monochloride, C_2Cl_2, analogous to ethine or acetylene, is obtained by passing the vapour of chloroform or of carbon-dichloride through a red-hot tube. It forms white needles, subliming between 175° and 200°.

NITROPARAFFINS, $C_nH_{2n+1}(NO_2)$.

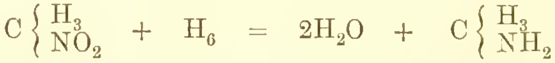
These compounds, isomeric with the nitrous ethers of the fatty series, are produced, together with the latter, by the action of silver nitrite on the iodoparaffins or alcoholic iodides,—nitromethane, for example, from methyl iodide :

$$H_3CI + AgNO_2 = AgI + H_3CNO_2.$$

They are also formed by the action of nitrogen tetroxide, or of fuming nitric acid, on the hydrocarbons of the ethene series ;

$$\underset{\text{Ethene.}}{C_2H_4} + N_2O_4 = \underset{\text{Dinitroethane.}}{C_2H_4(NO_2)_2}$$

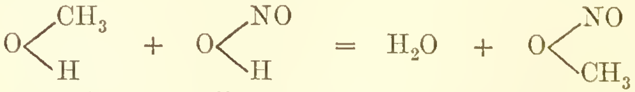
They have their nitrogen-atom in direct union with a carbon-atom, and are consequently converted by nascent hydrogen (evolved from water by sodium-amalgam) into amidoparaffins or amines ; *e.g.*,



$$C\left\{\begin{matrix}H_3\\NO_2\end{matrix}\right. + H_6 = 2H_2O + C\left\{\begin{matrix}H_3\\NH_2\end{matrix}\right.$$

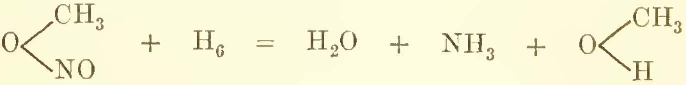
Nitromethane. Methylamine.

The nitrous ethers, on the other hand, which are formed by the action of nitrous acid on the corresponding alcohols, have their nitrogen united with carbon, only through the medium of oxygen ; *e.g.*,



Methyl alcohol. Nitrous acid. Methyl nitrite.

and are accordingly converted by nascent hydrogen into ammonia and the corresponding alcohols ; *e.g.*,



Methyl nitrite. Methyl alcohol.

The nitroparaffins are mostly decomposed, with explosion, when rapidly heated. They are not decomposed by potash or soda, whereas the nitrous ethers are quickly resolved thereby into nitrous acid and the corresponding alcohols.

Nitromethane, $CH_3.NO_2$, is formed, as above stated, by the action of silver nitrite on methyl iodide. The action is very violent, and the whole of the methyl iodide is converted into nitromethane, without a trace of the isomeric methyl nitrite. It is also formed by heating the potassium salt of monochloracetic acid with potassium nitrite :

$$2(CH_2Cl.CO_2K) + 2NO_2K + H_2O = 2(CH_3.NO_2) + CO_3K_2 + 2KCl + CO_2$$

Nitromethane is a heavy oil, having a peculiar odour, and boiling at 99–101°. When treated with an alcoholic solution of soda, it yields transparent needles of the sodium derivative, $CH_2Na(NO_2)$, the aqueous solution of which gives characteristic precipitates with various metallic solutions.

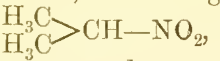
Bromonitromethane, $CH_2Br.NO_2$, formed by the action of bromine on the dry sodium-compound, is a heavy, pungent, strongly refracting liquid, boiling at 143–144°.

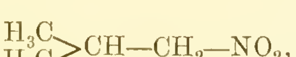
Nitroethane, $C_2H_5NO_2 = CH_3—CH_2—NO_2$, prepared like the methane-derivative, is a colourless, strongly-refracting liquid, having a fragrant ethereal odour, a specific gravity = 1·0582 at 13°, and boiling at 111–113° (ethyl nitrite boils at 16°). The vapour is inflammable, and burns with a pale yellow flame, but does not explode, even when heated above its boiling point. By nascent hydrogen it is converted into amidethane or ethylamine, $C_2H_5.NH_2$.

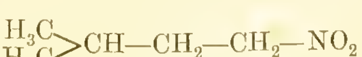
Bromonitroethane, $C_2H_4Br.NO_2$, and *dibromonitroethane*, $C_2H_3Br_2.(NO_2)$, are formed by the action of bromine on sodium-nitroethane. The former is a heavy acid oil, boiling at 145°–148°, the latter a mobile neutral liquid, boiling at 162°–164°.

Nitropropanes, $C_3H_7NO_2$.—There are two isomeric bodies having this composition, obtained by the action of silver nitrite on the iodides of normal propyl and pseudopropyl respectively.

Nitropropane, $CH_3—CH_2—CH_2—NO_2$, is a limpid mobile liquid, very little heavier than water, and boiling at 122°–127°.

Pseudo-nitropropane,  $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right>CH—NO_2$, boils at 112–117°. Both form crystalline sodium-compounds.

Nitro-isobutane, $C_4H_9NO_2$ =  $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right>CH—CH_2—NO_2$, from isobutyl iodide, is an oil smelling like peppermint, boiling at 135°–140°, and converted by nascent hydrogen into isobutylamine.

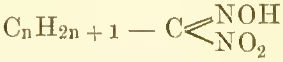
Nitro-isopentane, $C_5H_{11}NO_2$ =  $\left.\begin{matrix}H_3C\\H_3C\end{matrix}\right>CH—CH_2—CH_2—NO_2$, formed by the action of silver nitrite on ordinary amyl iodide, boils at 155–160°.

Reactions of Nitroparaffins with Metallic Salts.—The following table exhibits the reactions of various metallic salts with the sodium-compounds of nitromethane, nitro-ethane, and the two nitropropanes, which are sufficiently characteristic to be used for distinguishing these compounds one from the other.

	Sodium-derivative of			
	Nitromethane.	Nitro-ethane.	Nitropropane.	Pseudonitropropane.
Mercuric chloride,	Light yellow precipitate; explosive.	White crystalline precipitate.	White crystalline precipitate.	White crystalline precipitate.
Mercurous nitrate,	Black flocculent precipitate.	Dirty grey precipitate.	Black flocculent precipitate.	Black flocculent precipitate.
Ferric chloride,	Dark brownish red precipitate.	Blood-red coloration.	Blood-red solution.	Blood-red solution.
Cupric sulphate,	Grass-green precipitate.	Deep green solution.	Deep green solution.	Deep green solution.
Lead acetate,	White precipitate.	0	White precipitate.	0
Silver nitrate,	White precipitate, almost immediately turning black.	White precipitate, soon turning brown.	White precipitate, gradually turning brown.	Light yellow precipitate, soon turning black.

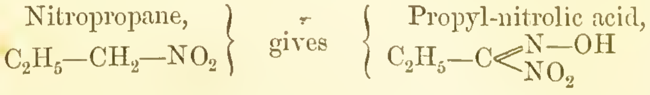
Action of Nitrous Acid on the Nitroparaffins.—The reactions of these bodies with nitrous acid (or better, with potassium nitrite and sulphuric acid) differ considerably, according as they contain primary, secondary, or tertiary alcohol-radicles (p. 44).

On treating the nitro-compounds of the primary alcohol radicles, in which the NO_2-group is united to the group CH_2, with potassium nitrite and dilute sulphuric acid, the solution acquires a deep red colour, and compounds called nitrolic acids, having the general formula,



$$C_nH_{2n+1} - C\Big\langle\begin{matrix}NOH\\ NO_2\end{matrix}$$

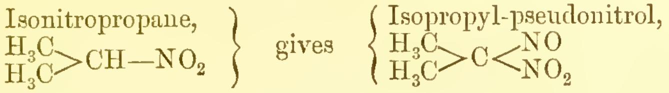
are produced by substitution of nitrosyl, NO, for one of the hydrogen-atoms in the group, CH_2; thus,



$$\left.\begin{matrix}\text{Nitropropane,}\\ C_2H_5-CH_2-NO_2\end{matrix}\right\}\ \text{gives}\ \left\{\begin{matrix}\text{Propyl-nitrolic acid,}\\ C_2H_5-C\Big\langle\begin{matrix}N-OH\\ NO_2\end{matrix}\end{matrix}\right.$$

The nitrolic acids are colourless, crystalline bodies, soluble in ether. Their alkali-salts have a deep red colour: hence the red tint produced at the commencement of the reaction above mentioned, and disappearing when the sulphuric acid is added in excess.

The nitro-compounds of the secondary alcohol-radicles, in which the NO_2 is linked to the group CH, give when similarly treated, deep blue solutions, which after a while deposit colourless compounds called pseudonitrols ; *e.g.*,



$$\left.\begin{array}{l}\text{Isonitropropane,}\\ \begin{matrix}H_3C\\H_3C\end{matrix}\!>CH{-}NO_2\end{array}\right\}\ \text{gives}\ \left\{\begin{array}{l}\text{Isopropyl-pseudonitrol,}\\ \begin{matrix}H_3C\\H_3C\end{matrix}\!>C<\!\begin{matrix}NO\\NO_2\end{matrix}\end{array}\right.$$

These compounds are colourless in the solid state, dark blue in the fused state or in solution.

The nitro-compounds of the tertiary alcohol-radicles, in which the NO_2-group is associated only with carbon: *e.g.* $(CH_3)_3C.NO_2$, are neither decomposed nor coloured by nitrous acid.

These reactions afford a characteristic and delicate test for distinguishing the primary, secondary, and tertiary alcohol-radicles (in their iodides) from one another.

Nitroparaffins of Higher Orders.

Trinitromethane or **Nitroform,** $CH(NO_2)_3$ is produced by the action of nitric acid on various organic compounds, but is most conveniently obtained as an ammonium salt, $C(NO_2)_3NH_4$, by the action of water or alcohol on trinitracetonitril or cyanotrinitromethane : $C(NO_2)_3CN + 2H_2O = C(NO_2)_3NH_4 + CO_2$; and on treating the yellow crystalline salt thus formed with strong sulphuric acid, nitroform is obtained in the free state.

Nitroform, at temperatures above 15°, is a colourless oil ; below that temperature it solidifies in colourless cubic crystals. It is moderately soluble in water, forming a dark yellow solution. It cannot be distilled, as it explodes with violence when heated.

The atom of hydrogen in nitroform may be replaced either by metals or by chlorous radicles, namely, bromine and nitryl. The metallic derivatives or *salts of nitroform*, are for the most part yellow and crystallisable : they explode when heated.

Bromonitroform, $C(NO_2)_3Br$, produced by exposing nitroform to the action of bromine for some days under the influence of direct sunshine, or more easily by treating an aqueous solution of mercuric nitroform, $C_2(NO_2)_6Hg$, with bromine, is a colourless liquid above +12°, but solidifies below that temperature to a white crystalline mass. It is somewhat soluble in water, and may be distilled with aqueous vapour, or in a current of air. It decomposes at 140°.

Tetranitromethane, $C(NO_2)_4$, is produced by treating nitroform with fuming nitric and sulphuric acids, heating the liquid to 100°, and passing air through it. A liquid then distils over, from which water throws down tetranitromethane as a heavy oil.

Tetranitromethane is liquid at ordinary temperatures, but solidifies at +13° to a white crystalline mass. It is insoluble in water, but soluble in alcohol and ether. It boils at 126°, and unlike nitroform, may be distilled without decomposition. When quickly heated it decomposes, with evolution of nitrous vapours, but without explosion. It does not take fire by contact with flame, but a glowing coal on which it is poured burns with a bright light.

Nitrotrichloromethane, Nitrochloroform or **Chloropicrin,** $C(NO_2)Cl_3$, is produced by the action of nitric acid on various chlorinated organic compounds—chloral, for example ; also by that of chlorine or hypochlorites on nitro-compounds, such as fulminating silver, $C_2N_2O_2\ Ag_2$, and picric acid, $C_6H_3(NO_2)_3O$. To prepare it, 10 parts of freshly prepared bleaching powder, made into a thick paste with water, are introduced into a retort, and a saturated solution of 1 part of picric acid heated to 30° is added. Reaction then generally takes place, without further heating, and the chloropicrin distils over with vapour of water.

Chloropicrin is a colourless liquid, having a specific gravity of 1·665, and boiling at 112°. It has a very pungent odour, and explodes when suddenly heated. By the action of nascent hydrogen (evolved by the action of iron on acetic acid) it is reduced to amidomethane or methylamine :

$$CCl_3.NO_2 + 12H = CH_3.NH_2 + 3HCl + 2H_2O.$$

Bromopicrin, $C(NO_2)Br_3$, is formed in like manner by heating picric acid with calcium hypobromite (slaked lime and bromine). It closely resembles chloropicrin, solidifies below +10° ; and may be distilled in a vacuum without decomposition.

Dinitrodichloromethane, $C(NO_2)_3Cl_2$ (commonly called *Marignac's oil),* obtained by distilling chloronaphthalene with nitric acid, is very much like chloropicrin.

AMIDOPARAFFINS.

These are derivatives formed by the replacement of 1, 2, or more hydrogen-atoms in a paraffin by the monatomic radicle amidogen, NH_2 ; *e.g.*,

Amido-ethane, $C_2H_5NH_2$
Diamido-ethane, $C_2H_4(NH_2)_2$

They are volatile and strongly basic compounds, exhibiting in their behaviour with acids and other bodies the closest resemblance to ammonia : they may indeed be regarded as derived from one or more molecules of ammonia by the substitution of alcohol-radicles, mono- or polyatomic, for equivalent quantities of hydrogen : hence they are called amines; *e.g.*,

$$\text{Amidoethane} = N\left\{\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right. \quad \text{Ethylamine.}$$

$$\text{Diamidoethane} = N_2\left\{\begin{matrix} (C_2H_4)'' \\ H_4 \end{matrix}\right. \quad \text{Ethene-diamine.}$$

The mono-derivatives are formed by the action of reducing agents on the mono-nitroparaffins: nitroethane, for example, treated with iron and acetic acid, is converted into ethylamine:

$$C_2H_5(NO_2) + H_6 = 2H_2O + C_2H_5NH_2 .$$

But they are more readily prepared by other methods, which, together with the properties and reactions of these bodies, will be discussed in a future chapter.

AZOPARAFFINS, NITRILS, or CYANIDES,

$C_nH_{2n-1}N$.

These compounds may be regarded as derived from the paraffins by substitution of trivalent nitrogen for 3 atoms of hydrogen, or as compounds of nitrogen with trivalent radicles, C_nH_{2n-1} (nitrils), or as compounds of the univalent radicle, $C{\equiv}N$— (cyanogen) with a univalent radicle, $C_{n-1}H_{2n-1}$ or C_pH_{2p+1};* *e.g.*,

Azomethane, Methenyl Nitril, or Hydrogen Cyanide,	$N{\equiv}C{-}H$.
Azoethane, Ethenyl Nitril, or Methyl Cyanide,	$N{\equiv}C{-}CH_3$.
Azopropane, Propenyl Nitril, or Ethyl Cyanide,	$N{\equiv}C{-}C_2H_5$.

There are also cyanides derived from hydrocarbons belonging to the aromatic group, *e.g.*, phenyl cyanide, $C_7H_5N = C_6H_5.CN$, from toluene, C_7H_8.

Cyanogen is obtained in the free state, as already described (i. 185) by the action of heat on mercuric cyanide. It is a colourless, inflammable gas, of specific gravity 26 ($H = 1$.) Its molecular weight is therefore 52, and it is represented by the formula,

$$C_2N_2 = N{\equiv}C{-}C{\equiv}N ,$$

which gives $2 \times 12 + 2 \times 14 = 52$.

The univalent radicle, CN, is often represented by the shorter formula Cy.

In the preparation of cynogen from mercuric cyanide, a brownish or blackish substance, called paracyanogen, is always formed in small quantity. It is insoluble in water, and when calcined in a gas which does not act upon it, such as nitrogen or carbon dioxide, is completely volatilised in the form of cyanogen gas, without leaving any carbonaceous residue: hence it appears to be isomeric or polymeric with cyanogen.

Hydrogen Cyanide; Hydrocyanic or **Prussic Acid,** HCN.—This very important compound, so remarkable for its poisonous properties, was discovered as early as 1782 by Scheele.

Pure anhydrous hydrocyanic acid may be obtained by passing dry sulphuretted hydrogen gas over dry mercuric cyanide, gently heated in a glass tube connected with a small receiver cooled by a freezing mixture. It is a thin, colourless, and exceedingly volatile liquid, which has a density of 0·7058 at 7·2°, boils at 26·1°, and solidifies when cooled to $-18°$: its odour is very powerful and most characteristic, much resembling that of peach-blossoms or bitter almond-oil; it has a very feeble acid reaction, and mixes with water and alcohol in all proportions. In the anhydrous state this substance constitutes one of the most formidable poisons known, and even when largely diluted with water, its effects upon the animal system are exceedingly energetic: it is employed, however, in medicine, in very small doses. The inhalation of the vapour should be carefully avoided in all experiments in which hydrocyanic acid is concerned, as it produces headache, giddiness, and other disagreeable symptoms; ammonia and chlorine are the best antidotes.

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* If $n-1 = p$, $2n-1 = 2p+1$.

The acid in its pure form can scarcely be preserved; even when enclosed in a carefully stoppered bottle, it is observed after a very short time to darken, and eventually to deposit a black substance containing carbon, nitrogen, and perhaps hydrogen: ammonia is formed at the same time, and many other products. Light favours this decomposition. Even in the dilute state it is apt to decompose, becoming brown and turbid, but not always with the same facility, some samples resisting change for a great length of time, and then solidifying in a few weeks to a brown, pasty mass.

When hydrocyanic acid is mixed with concentrated mineral acids, hydrochloric acid, for example, the whole solidifies to a crystalline paste of sal-ammoniac and formic acid:

$$CNH + 2H_2O = NH_3 + CH_2O_2.$$

On the other hand, when dry ammonium formate is heated to 200°, it is almost entirely converted into hydrocyanic acid and water.

Aqueous solution of hydrocyanic acid may be prepared by various means. The most economical, and by far the best, where considerable quantities are wanted, is to decompose yellow potassium ferrocyanide at boiling heat with dilute sulphuric acid. 500 grains of the powdered ferrocyanide, K_4FeCy_6, are dissolved in four or five ounces of warm water, and introduced into a capacious flask or globe, connected by a perforated cork and wide bent tube with a Liebig's condenser well supplied with cold water; 300 grains of oil of vitriol are diluted with three or four times as much water and added to the contents of the flask; and the distillation is carried on till about half the liquid has distilled over, after which the process may be interrupted. The residue in the retort is a white or yellow mass, consisting of potassio-ferrous ferrocyanide, $K_2Fe_2Cy_6$ (see p. 89), mixed with potassium sulphate:

$$2K_4Fe''Cy_6 + 3H_2SO_4 = 6HCy + K_2Fe''_2Cy_6 + 3K_2SO_4.$$

When hydrocyanic acid is wanted for the purposes of pharmacy, it is best to prepare a strong solution in the manner above described, and then, having ascertained its exact strength, to dilute it with pure water to the standard of the Pharmacopœia, viz., 2 per cent. of real acid. This examination is best made by precipitating with excess of silver nitrate a known weight of the acid to be tried, collecting the insoluble silver cyanide upon a small filter previously weighed, then washing, drying, and lastly, reweighing the whole. From the weight of the cyanide that of the hydrocyanic acid can be easily calculated, a molecule of the one ($CNAg = 134$), corresponding with a molecule of the other ($CNH = 27$); or the weight of the silver cyanide may be divided by 5, which will give a close approximation to the truth.

Another very good method for determining the amount of hydrocyanic acid in a liquid has been suggested by Liebig. It is based upon the property possessed by potassium cyanide of dissolving a quantity of silver cyanide sufficient to produce with it a double cyanide, KCy.AgCy. Hence a solution of hydrocyanic acid, which is supersaturated with potash, and mixed with a few drops of solution of common salt, will not yield a permanent precipitate with silver nitrate before the whole of the hydrocyanic acid is converted into the above double salt. If we know the amount of silver in a given volume of the nitrate solution, it is easy to calculate the quantity of hydrocyanic acid; for this quantity will stand to the amount of silver in the nitrate consumed, as 2 molecules of hydrocyanic acid to 1 atom of silver, *i.e.:*

$$108 : 54 = \text{silver consumed} : x.$$

It is a common remark, that the hydrocyanic acid made from potassium ferrocyanide keeps better than that made by other means. The cause of this is ascribed to the presence of a trace of mineral acid. Everitt found that a few drops of hydrochloric acid, added to a large bulk of the pure dilute acid, preserved it from decomposition, while another portion, not so treated, became completely spoiled.

A very convenient process for the extemporaneous preparation of an acid of definite strength, is to decompose a known quantity of potassium cyanide with solution of tartaric acid: 100 grains of crystallised tartaric acid in powder, 44 grains of potassium cyanide, and 2 measured ounces of distilled water, shaken up in a phial for a few seconds, and then left at rest, in order that the precipitate may subside, will yield an acid of very nearly the required strength. A little alcohol may be added to complete the separation of the cream of tartar; no filtration or other treatment need be employed.

Bitter almonds, the kernels of plums and peaches, the seeds of the apple, the leaves of the cherry-laurel, and various other parts of plants belonging to the great natural order *Rosaceæ*, yield on distillation with water a sweet-smelling liquid containing hydrocyanic acid. This is probably due in all cases to the decomposition of a substance called amygdalin under the influence of emulsin or synaptase, a nitrogenised ferment present in the organic structure (see GLUCOSIDES). The reaction is expressed by the equation :

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Prussic acid.}}{CNH} + \underset{\text{Bitter almond oil.}}{C_7H_8O} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Hydrocyanic acid exists ready formed to a considerable extent in the juice of the bitter cassava.

The presence of hydrocyanic acid is detected with the utmost ease : its remarkable odour and high degree of volatility almost sufficiently characterise it. With solution of silver nitrate it gives a dense curdy white precipitate, much resembling the chloride, but differing from that substance in not blackening so readily by light, in being soluble in boiling nitric acid, and in suffering complete decomposition when heated in the dry state, metallic silver being left: the chloride, under the same circumstances, merely fuses, but undergoes no chemical change. The production of Prussian blue by "Scheele's test" is an excellent and most decisive experiment, which may be made with a very small quantity of the acid. The liquid to be examined is mixed with a few drops of solution of ferrous sulphate and an excess of caustic potash, and the whole exposed to the air for 10 or 15 minutes, with agitation, whereby the ferrous salt is partly converted into ferric salt: hydrochloric acid is then added in excess, which dissolves the precipitated iron oxide, and, if hydrocyanic acid is present, leaves Prussian blue as an insoluble powder. The reaction will be explained in connection with the ferrocyanides (p. 89).

Another very delicate test for hydrocyanic acid will be mentioned in connection with thiocyanic acid.

Metallic Cyanides.—The most important of the metallic cyanides are the following: they bear the most perfect analogy to the haloïd-salts.

Potassium Cyanide, CNK or KCy.—Potassium heated in cyanogen gas, takes fire and burns in a very beautiful manner, yielding potassium cyanide: the same substance is produced when potassium is heated in the vapour of hydrocyanic acid, hydrogen being liberated. When pure nitrogen is transmitted through a white-hot tube containing a mixture of potassium carbonate and charcoal, a small quantity of potassium cyanide is formed, which settles on the cooler portions of the tube as a white amorphous powder: carbon monoxide is at the same time evolved.* When azotised organic matter of any kind, capable of furnishing ammonia by destructive distillation, as horn-shavings, parings of hides, &c., is heated to redness with potassium carbonate in a close vessel, a very abundant production of potassium cyanide results, which cannot, however, be advantageously extracted by direct means, but in practice is always converted into ferrocyanide, which is a much more stable substance, and crystallises better.

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* According to the experiments of Margueritte and De Sourdeval, the formation of cyanide appears to be more abundant if the potash be replaced by baryta. If the barium cyanide thus formed be exposed to a stream of superheated steam at 300° C. the nitrogen of the salt is eliminated in the form of ammonia. Margueritte and De Sourdeval recommend this process as a method of preparing ammonia by means of atmospheric nitrogen.

Potassium cyanide may be prepared by passing the vapour of hydrocyanic acid into a cold alcoholic solution of potash: the salt is then deposited in the crystalline form, and may be separated from the liquid, pressed and dried. But it is more generally made from the ferrocyanide, which, when heated to whiteness in a nearly close vessel, evolves nitrogen and other gases, and leaves a mixture of carbon, iron carbide, and potassium cyanide, which latter salt is not decomposed unless the temperature is excessively high.

Liebig has given a very easy and excellent process for making potassium cyanide, which does not, however, yield it pure, but mixed with potassium cyanate. For most of the applications of potassium cyanide, electro-plating and gilding, for example, for which a considerable quantity is now required, this impurity is of no consequence. Eight parts of potassium ferrocyanide are rendered anhydrous by gentle heat, and intimately mixed with three parts of dry potassium carbonate: this mixture is thrown into a red-hot earthen crucible, and kept in fusion, with occasional stirring, until gas ceases to be evolved, and the fluid portion of the mass becomes colourless. The crucible is left at rest for a moment, and then the clear salt is decanted from the heavy black sediment at the bottom, which is principally metallic iron in a state of minute division. The reaction is represented by the equation:

$$\underset{\text{Ferrocyanide.}}{K_4FeCy_6} + \underset{\text{Carbonate.}}{K_2CO_3} = \underset{\text{Cyanide.}}{5KCy} + \underset{\text{Cyanate.}}{KCyO} + Fe + CO_2.$$

The product may be advantageously used, instead of potassium ferrocyanide, in the preparation of hydrocyanic acid, by distillation with diluted oil of vitriol.

Potassium cyanide is often produced in considerable quantity in blast furnaces in which iron ores are smelted with coal or coke.

Potassium cyanide forms colourless, cubic or octohedral, anhydrous crystals, deliquescent in the air, and exceedingly soluble in water: it dissolves in boiling alcohol, but separates in great measure on cooling. It is readibly fusible, and undergoes no change at a moderate red or even white heat, when excluded from air; otherwise, oxygen is absorbed and the cyanide becomes cyanate. Its solution always has an alkaline reaction, and when exposed to the air exhales the odour of hydrocyanic acid: it is decomposed by the weakest acids, even the carbonic acid of the air, and when boiled in a retort is slowly converted into potassium formate, with separation of ammonia. It is said to be as poisonous as hydrocyanic acid itself.

Sodium Cyanide, NaCy, is a very soluble salt, corresponding closely with the foregoing, and obtained by similar means.

Ammonium Cyanide, NH_4Cy, is a colourless, crystallisable, and very volatile substance, prepared by distilling a mixture of potassium cyanide and sal-ammoniac; or by mingling the vapour of anhydrous hydrocyanic acid with ammoniacal gas; or, lastly, by passing ammonia over red-hot charcoal. It is very soluble in water, subject to spontaneous decomposition, and is slightly poisonous.

Mercuric Cyanide, $Hg(CN)_2$, or $HgCy_2$.—One of the most remarkable properties of cyanogen is its powerful attraction for certain of the less oxidable metals, as silver, and more particularly for mercury and palladium. Dilute hydrocyanic acid dissolves finely powdered mercuric oxide with the utmost ease: the liquid loses all odour, and yields on evaporation crystals of mercuric cyanide. Potassium cyanide is in like manner decomposed by mercuric oxide, potassium hydroxide being produced. Mercuric cyanide is generally prepared from potassium ferrocyanide; 2 parts of the salt are dissolved in 15 parts of hot water, and 3 parts of dry mercuric sulphate are added; the whole is boiled for 15 minutes, and filtered hot from the iron oxide, which separates. The solution, on cooling, deposits the mercuric cyanide in crystals. Mercuric cyanide forms white, translucent, dimetric prisms, much resembling those of corrosive sublimate: it is soluble in 8 parts of cold water, and in a much smaller quantity at a higher temperature, also in alcohol. The solution has a disagreeable metallic taste, is very poisonous, and is not precipitated by alkalis. Mercuric cyanide is used in the laboratory as a source of cyanogen.

Silver Cyanide, $AgCy$, has been already described (p. 84).—*Zinc cyanide*, $ZnCy_2$, is a white insoluble powder, prepared by mixing zinc acetate with hydrocyanic acid.—*Cobalt cyanide*, $CoCy_2$, is obtained by similar means: it is dirty-white, and insoluble.—*Palladium cyanide*, $PdCy_2$, forms a yellowish-white precipitate when the chloride of that metal is mixed with a soluble cyanide.—*Auric cyanide*, $AuCy_3$, is yellowish-white and insoluble, but freely dissolved by solution of potassium cyanide.

Iron Cyanides.—These compounds are scarcely known in the separate state, on account of their great tendency to form double salts. On adding potassium cyanide to a ferrous salt, a yellowish-red flocculent precipitate is formed, consisting chiefly of ferrous cyanide, $FeCy_2$, but always containing a certain quantity of potassium cyanide, and dissolved as ferrocyanide by excess of that salt. Ferric cyanide, Fe_2Cy_6, is known only in solution. Pelouze obtained an insoluble green compound containing Fe_3Cy_8, or $FeCy_2.Fe_2Cy_6$, by passing chlorine gas into a boiling solution of potassium ferrocyanide.

The iron cyanides unite with other metallic cyanides, forming two very important groups of compounds, called ferrocyanides and ferricyanides, the composition of which may be illustrated by the respective potassium-salts:

Ferrocyanide, ... $K_4Fe''Cy_6$, or $4KCy.Fe''Cy_2$
Ferricyanide, ... $K_3Fe'''Cy_6$. or $3KCy.Fe'''Cy_3$.

It will be seen from these formulæ, that ferro- and ferricyanides containing the same quantity of cyanogen, differ from one another only by one atom of univalent metal, and, accordingly, it is found that the former may be converted into the latter, by the action of oxidising (metal-abstracting) agents, and the latter into the former by the action of reducing (metal adding) agents. Thus potassium ferrocyanide is easily converted into the ferricyanide by the action of chlorine, and many double ferrocyanides may be formed from ferricyanides by the action of alkalis in presence of a reducing agent; thus potassium ferricyanide, $K_3Fe'''Cy_6$, is easily converted into ammonio-tripotassic ferrocyanide $(NH_4)K_3Fe''Cy_6$, by the action of ammonia in presence of glucose.*

Ferrocyanides.

Potassium Ferrocyanide, K_4FeCy_6, or $4KCy.FeCy_2$, commonly called *yellow prussiate of potash.*—This important salt is formed—1. By digesting precipitated ferrous cyanide in aqueous solution of potassium cyanide. 2. By digesting ferrous hydrate with potassium cyanide, potash being formed at the same time:

$$6KCy + FeH_2O_2 = 2KHO + K_4FeCy_6.$$

3. Ferrous cyanide with aqueous potash:

$$3FeCy_2 + 4KHO = 2FeH_2O_2 + K_4FeCy_6.$$

4. Aqueous potassium cyanide with metallic iron: if the air be excluded, hydrogen is evolved:

$$6KCy + Fe + 2H_2O = K_4FeCy_6 + 2KHO + H_2;$$

but if the air has access to the liquid, oxygen is absorbed, and no hydrogen is evolved:

$$6KCy + Fe + H_2O + O = K_4FeCy_6 + 2KHO.$$

5. Ferrous sulphide with aqueous potassium cyanide:

$$6KCy + FeS = K_2S = K_4FeCy_6.$$

6. Any soluble ferrous salt with potassium cyanide; *e.g.:*

$$6KCy + FeSO_4 = K_2SO_4 + K_4FeCy_6.$$

Potassium ferrocyanide is manufactured on the large sale by the following process:—Dry refuse animal matter of any kind is fused at a red heat with impure potassium carbonate and iron filings, in a large iron vessel from which the air should be excluded as much as possible; potassium cyanide is generated in large quantity. The melted mass is afterwards treated with hot water, which dissolves out the cyanide and other salts, the cyanide being quickly converted by the oxide or sulphide* of iron into ferrocyanide. The filtered solution is evaporated, and the first-formed crystals are purified by re-solution. If a sufficient quantity of iron be not present, great loss is incurred by the decomposition of the cyanide into potassium carbonate and ammonia.

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* The ferrocyanides and ferricyanides are sometimes regarded as salts of peculiar compound radicles containing iron, viz., *ferrocyanogen*, $Fe''Cy_6$, and *ferricyanogen*, $Fe'''Cy_6$, the first being quadrivalent, the second trivalent; but there is nothing gained by this assumption. For a discussion of the formulæ of these salts, and of the double cyanides in general, see Watts's Dictionary of Chemistry, vol. ii. p. 201.

A new process for the preparation of potassium ferrocyanide has lately been proposed by Gélis. It consists in converting carbon bisulphide into ammonium thiocarbonate by agitating it with ammonium sulphide: $CS_2 + (NH_4)_2S = (NH_4)_2CS_3$, and heating the product thus obtained with potassium sulphide, whereby potassium thiocyanate (p. 102) is formed, with evolution of ammonium sulphide and hydrogen sulphide:

$$2(NH_4)_2CS_3 + K_2S = 2KCNS + 2(NH_4)HS + 3H_2S.$$

The potassium thiocyanate is dried, mixed with finely divided metallic iron, and heated for a short time in a closed iron vessel to dull redness, whereby the mixture is converted into potassium ferrocyanide, potassium sulphide, and iron sulphide:

$$6KCyS + Fe_6 = K_4FeCy_6 + 5FeS + K_2S.$$

By treatment with water, the sulphide and ferrocyanide of potassium are dissolved, and on evaporation the ferrocyanide is obtained in crystals. It remains to be seen whether this ingenious process is capable of being carried out upon a large scale.

Potassium ferrocyanide forms large, transparent, yellow crystals, $K_4FeCy_6 + 3aq.$, derived from an octohedron with a square base: they cleave with facility in a direction parallel to the base of the octohedron, and are tough and difficult to powder. They dissolve in 4 parts of cold and 2 parts of boiling water, and are insoluble in alcohol. They are permanent in the air, and have a mild saline taste. The salt has no poisonous properties, and, in small doses at least, is merely purgative. Exposed to a gentle heat, it loses 3 molecules of water, and becomes anhydrous: at a high temperature it yields potassium cyanide, iron carbide, and various gaseous products; if air be admitted, the cyanide becomes cyanate.

Potassium ferrocyanide is a chemical reagent of great value: when mixed in solution with neutral or slightly acid salts of the heavy metals, it gives rise to precipitates which very frequently present highly characteristic colours. In most of these compounds the potassium is simply displaced by the new metal: the beautiful brown ferrocyanide of copper contains, for example, Cu_2FeCy_6, or $2CuCy_2.FeCy_2$, and that of lead, Pb_2FeCy_6.

With *ferrous salts*, potassium ferrocyanide gives a precipitate which is perfectly white, if the air be excluded and the solution is quite free from ferric salt, but quickly turns blue on exposure to the air. It consists of potassio-ferrous ferrocyanide, $K_2Fe_2Cy_6$, or potassium ferrocyanide having half the potassium replaced by iron. The same salt is produced in the preparation of hydrocyanic acid by distilling potassium ferrocyanide with dilute sulphuric acid (p. 82).

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* The sulphur is derived from the reduced sulphate of the crude pearl-ashes and the animal substances used in the manufacture.

When a soluble ferrocyanide is added to the solution of a *ferric salt*, a deep blue precipitate is formed, consisting of ferric ferrocyanide, Fe_7Cy_{18}, or $Fe'''_4Fe''_3Cy_{18}$, or $2(Fe_2)^{vi}Cy_6.3FeCy_2$, which in combination with 18 molecules of water constitutes ordinary Prussian blue. This beautiful pigment is best prepared by adding potassium ferrocyanide to ferric nitrate or chloride :

$$3K_4FeCy_6 + 2(Fe_2)^{vi}Cl_6 = 12KCl + Fe_7Cy_{18}.$$

It is also formed by precipitating a mixture of ferrous and ferric salts with potassium cyanide :

$$18KCy + 3FeCl_2 + 2(Fe_2)^{vi}Cl_6 = 18KCl + Fe_7Cy_{18}.$$

This reaction explains Scheele's test for prussic acid (p. 84). Prussian blue is also formed by the action of air, chlorine-water, and other oxidising agents, on potassio-ferrous ferrocyanide ; probably thus :

$$6K_2Fe_2Cy_6 + O_3 = Fe_7Cy_{18} + 3K_4FeCy_6 + Fe_2O_3.$$

It is chiefly by this last reaction that Prussian blue is prepared on the large scale, potassium ferrocyanide being first precipitated by ferrous sulphate, and the resulting white or light blue precipitate either left to oxidise by contact with the air, or subjected to the action of nitric acid, chlorine, hypochlorites, chromic acid, &c. The product, however, is not pure ferric ferrocyanide : for it is certain that another and simpler reaction takes place at the same time, by which the potassio-ferrous ferrocyanide, $(K_2Fe'')Fe''Cy_6$, is converted, by abstraction of an atom of potassium, into potassio-ferrous ferricyanide, $(KFe'')Fe'''Cy_6$, which also possesses a fine deep-blue colour. Commercial Prussian blue is therefore generally a mixture of this compound with ferric ferrocyanide, $Fe'''_4Fe''_3Cy_{18}$, the one or the other predominating according to the manner in which the process is conducted.

Prussian blue in the moist state forms a bulky precipitate, which shrinks to a comparatively small compass when well washed and dried by a gentle heat. In the dry state it is hard and brittle, much resembling in appearance the best indigo : the freshly fractured surfaces have a beautiful copper-red lustre, similar to that produced by rubbing indigo with a hard body. Prussian blue is quite insoluble in water and dilute acids, with the exception of oxalic acid, in a solution of which it dissolves, forming a deep-blue liquid, which is sometimes used as ink : concentrated oil of vitriol converts it into a white, pasty mass, which again becomes blue on addition of water. Alkalis destroy the colour instantly: they dissolve out a ferrocyanide, and leave ferric oxide. Boiled with water and mercuric oxide, it yields mercuric cyanide and ferric oxide. Heated in the air, Prussian blue burns like tinder, leaving a residue of ferric oxide. Exposed to a high temperature in a close vessel, it gives off water, ammonium cyanide, and ammonium carbonate, and leaves carbide of iron. It forms a very beautiful pigment, both as oil and water colour, but has little permanency.

Common or basic Prussian blue is an inferior article, prepared by precipitating a mixture of ferrous sulphate and alum with potassium ferrocyanide, and exposing the precipitate to the air. It contains alumina, which impairs the colour, but adds to the weight.

Soluble Prussian blue is obtained by adding ferric chloride to an excess of potassium ferrocyanide; it is insoluble in the saline liquor, but soluble in pure water. It has a deep-blue colour, and probably consists of potassio-ferrous ferricyanide.

Hydrogen Ferrocyanide, or *Hydroferrocyanic Acid,* H_4FeCy_6, is prepared by decomposing ferrocyanide of lead or copper suspended in water by a stream of sulphuretted hydrogen gas, and separates on evaporating the filtered solution in a vacuum over oil of vitriol. Its solution in water has a powerfully acid taste and reaction, and decomposes alkaline carbonates with effervescence: it does not dissolve mercuric oxide in the cold, but when heat is applied, undergoes decomposition, forming mercuric cyanide and ferrous cyanide: $H_4FeCy_6 + 2HgO = 2HgCy_2 + FeCy_2 + 2H_2O$; but the ferrous cyanide is immediately oxidised by the excess of mercuric oxide, with separation of metallic mercury. In the dry state the acid is very permanent, but when long exposed to the air in contact with water, it is entirely converted into Prussian blue.

Sodium Ferrocyanide, $Na_4FeCy_6.12$ aq., crystallises in yellow four-sided prisms, which are efflorescent in the air, and very soluble.

Ammonium Ferrocyanide, $(NH_4)_4FeCy_6.3$ aq., is isomorphous with potassium ferrocyanide: it is easily soluble, and is decomposed by ebullition. *Barium Ferrocyanide,* Ba_2FeCy_6, prepared by boiling potassium ferrocyanide with a large excess of barium chloride, or Prussian blue with baryta-water, forms minute yellow, anhydrous crystals, which have but a small degree of solubility even in boiling water. The corresponding compounds of *strontium, calcium,* and *magnesium* are more freely soluble. The ferrocyanides of *silver, lead, zinc, manganese,* and *bismuth* are white and insoluble; those of *nickel* and *cobalt* are pale-green and insoluble; and lastly, that of *copper* has a beautiful reddish-brown tint.

There are also several double ferrocyanides. When, for example, concentrated solutions of calcium chloride and potassium ferrocyanide are mixed, a sparingly soluble crystalline precipitate falls, containing $K_2CaFeCy_6$.

Ferricyanides.

These salts are formed, as already observed, by abstraction of metal from the ferrocyanides; in other words, by the action of oxidising agents.

Potassium Ferricyanide, $K_3Fe'''Cy_6$, or $K_6(Fe_2)^{vi}Cy_{12}$, often called *red prussiate of potash,* is prepared by slowly passing chlorine, with agitation, into a somewhat dilute and cold solution of potassium ferrocyanide, until the liquid acquires a deep reddish green colour, and ceases to precipitate a ferric salt. The solution is evaporated until a skin begins to form upon the surface, then filtered and left to cool; and the salt is purified by re-crystallisation. It forms prismatic, or sometimes tabular crystals, belonging to the monoclinic system, of a beautiful ruby-red tint, permanent in the air, and soluble in 4 parts of cold water: the solution has a dark-greenish colour. The crystals burn and emit sparks when introduced into the flame of a candle. The salt is decomposed by excess of chlorine, and by deoxidising agents, as sulphuretted hydrogen.

Hydrogen ferricyanide is obtained in the form of a reddish-brown acid liquid, by decomposing lead ferricyanide with sulphuric acid: it is very unstable, and is resolved by boiling into hydrated ferric cyanide, an insoluble dark-green powder containing $Fe_2Cy_6.3\,aq.$, and hydrocyanic acid. The ferricyanides of *sodium, ammonium,* and of the *alkaline earth-metals,* are soluble; those of most of the other metals are insoluble. Potassium ferricyanide added to a ferric salt occasions no precipitate, but merely a darkening of the reddish-brown colour of the solution; with *ferrous salts,* on the other hand, it gives a deep blue precipitate, consisting of ferrous ferricyanide, $Fe_5Cy_{12}+x\,aq.$, or $Fe''_3(Fe_2)^{vi}Cy_{12}+x\,aq.$, which, when dry, has a brighter tint than Prussian blue: it is known under the name of *Turnbull's blue.* Hence, potassium ferricyanide is as delicate a test for ferrous salts as the yellow ferrocyanide is for ferric salts.

COBALTICYANIDES.—This name is applied to a series of compounds analogous to the preceding, containing cobalt in place of iron; a hydrogen-acid has been obtained, and a number of salts, which much resemble the ferricyanides. Several other metals of the same ismorphous family are found capable of replacing iron in these compounds.

NITROPRUSSIDES.—These are salts produced by the action of nitric acid upon ferrocyanides and ferricyanides. The general formula of these salts appears to be $M_2(NO)Fe''Cy_5$, which exhibits a close relation to those of the ferro- and ferricyanides.

The formation of the nitroprussides appears to consist in the reduction of the nitric acid to the state of nitrogen dioxide or nitrosyl, NO, which replaces 1 molecule of metallic cyanide, MCy, in a molecule of ferricyanide, $M_3Fe'''Cy_6$. The formation of these salts is attended with the production of a variety of secondary products, such as cyanogen, oxamide, hydrocyanic acid, nitrogen, carbonic acid, &c. One of the finest compounds of this series is the nitroprusside of sodium, $Na_2(NO)Fe''Cy_5 + 2\,aq.$, which is readily obtained by treating 2 parts of powdered potassium ferrocyanide with 5 parts of common nitric acid previously diluted with its own volume of water. The solution, after the evolution of gas has ceased, is digested on the water-bath, until ferrous salts no longer yield a blue, but a slate-coloured precipitate. The liquid is now allowed to cool, when much potassium nitrate, and occasionally oxamide, is deposited : it is filtered and neutralised with sodium carbonate, which yields a green or brown precipitate, and a ruby-coloured filtrate. This, on evaporation, gives a crystallisation of the nitrates of potassium and sodium, together with the nitroprusside. The crystals of the latter are selected and purified by crystallisation ; they are rhombic and of a splendid ruby colour. The soluble nitroprussides strike a most beautiful violet tint with soluble sulphides, affording an extremely delicate test for alkaline sulphides.

ALCOHOLIC CYANIDES OR HYDROCYANIC ETHERS.

These compounds play an important part in organic chemistry : for example, in the conversion of alcohols into acids containing a greater number of carbon-atoms.

The cyanides of univalent alcohol-radicles may also be regarded as compounds of nitrogen with trivalent radicles : hence, as already observed (p. 81), they are often called nitrils.

These alcoholic cyanides are produced :

1. By distilling a mixture of potassium cyanide and the potassium-salt of ethylsulphuric acid, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4$, or a similar acid :

$$KCN + (C_2H_5)KSO_4 = K_2SO_4 + C_2H_5.CN.$$

2. By the dehydrating action of phosphoric oxide on the ammonium-salts of the monobasic acids, $C_nH_{2n}O_2$ and $C_nH_{2n-8}O_2$, homologous with acetic and benzoic acid respectively, thus :

$$\begin{array}{cccc} \underset{\substack{\text{Ammonium}\\\text{acetate.}}}{C_2H_3O_2.NH_4} & - \; 2H_2O & = & \underset{\substack{\text{Ethenyl}\\\text{nitril.}}}{C_2H_3N} \\ \underset{\substack{\text{Ammonium}\\\text{benzoate.}}}{C_7H_5O_2.NH_4} & - \; 2H_2O & = & \underset{\text{Benzonitril.}}{C_7H_5N} \end{array}$$

The bodies obtained by these two processes are oily liquids, exhibiting the same properties whether prepared by the first or the second method, excepting that those obtained by the latter have an aromatic fragrant odour, whereas those prepared by the former have a pungent and repulsive odour, due to the presence of certain isomeric compounds, to be noticed further on. *Methyl cyanide, Ethenyl-nitril,* or *Acetonitril,* boils at 77° ; *Ethyl cyanide,* or *Propenyl-*

nitril, at 82° ; *Butyl cyanide*, or *Valeronitril*, at 125–128° ; *Isopentyl cyanide, Amyl cyanide*, or *Capronitril*, at 146°; *Phenyl cyanide*, or *Benzonitril*, at 190·6°.

All these cyanides, when heated with fuming sulphuric acid or sulphuric oxide, are converted into sulpho-acids; thus:

$$\underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3.CN} + H_2O + 2SO_4H_2 = SO_4H(NH_4) + \underset{\substack{\text{Sulphacetic}\\\text{acid.}}}{C_2H_4SO_5}$$

$$\underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3.CN} + 3H_2SO_4 = SO_4H(NH_4) + CO_2 + \underset{\substack{\text{Disulpho-}\\\text{metholic acid.}}}{CH_4S_2O_6}$$

By heating with caustic potash or soda, they are resolved into ammonia and the corresponding fatty or aromatic acid, just as hydrocyanic acid similarly treated is resolved into ammonia and formic acid ; thus:

$$\underset{\substack{\text{Hydrogen}\\\text{cyanide.}}}{HCN} + 2H_2O = NH_3 + \underset{\substack{\text{Formic}\\\text{acid.}}}{CH_2O_2}$$

$$\underset{\substack{\text{Ethyl}\\\text{cyanide.}}}{C_2H_5CN} + 2H_2O = NH_3 + \underset{\substack{\text{Propionic}\\\text{acid.}}}{C_3H_6O_2}$$

$$\underset{\substack{\text{Phenyl}\\\text{cyanide.}}}{C_6H_5CN} + 2H_2O = NH_3 + \underset{\text{Benzoic acid.}}{C_7H_6O_2}$$

The alcoholic cyanides or nitrils, treated with nascent hydrogen, are converted into the corresponding amine-bases, *e.g.:*

$$\underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CNCH_3} + 2H_2 = \underset{\text{Ethylamine.}}{NH_2(CH_2CH_3) \text{ or } C_2H_7N}$$

Ethene Cyanide, $(C_2H_4)''(CN)_2$, is obtained by distilling potassium cyanide with ethene bromide :

$$C_2H_4Br_2 + 2KCN = 2KBr + C_2H_4(CN)_2.$$

It is a crystalline body, melting at 50°, and converted by alcoholic potash into ammonia and succinic acid :

$$C_2H_4(CN)_2 + 4H_2O = 2NH_3 + C_4H_6O_4.$$

Isocyanides, or **Carbamines.**—On examining the equations just given for the decomposition of the alcoholic cyanides under the influence of alkalis, it is easy to see that the reaction might be supposed to take place in a different way, each cyanide yielding, not ammonia and an acid containing the same number of carbon-atoms as itself, but an alcoholic ammonia or amine, and formic acid ; thus :

$$\underset{\substack{\text{Ethyl}\\\text{cyanide}}}{C_2H_5.CN} + 2H_2O = \underset{\substack{\text{Ethyl-}\\\text{amine.}}}{NH_2C_2H_5} + \underset{\substack{\text{Formic}\\\text{acid.}}}{CH_2O_2}$$

In the one case the alcohol-radicle remains united with the carbon, producing a homologue of formic acid, together with ammonia; in the other it remains united with the nitrogen, producing a homologue of ammonia, together with formic acid.

A class of cyanides exhibiting the second of these reactions has been discovered by Dr Hofmann.* They are obtained by distilling a mixture of an alcoholic ammonia-base and chloroform with alcoholic potash; for example:

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Chloroform.}}{CHCl_3} = 3HCl + \underset{\text{Phenyl-isocyanide.}}{C_7H_5N}$$

The potash serves to neutralise the hydrochloric acid produced, which would otherwise quickly decompose the isocyanide. Phenyl-isocyanide, or phenyl-carbamine, when freed from excess of aniline by oxalic acid, then dried with caustic potash and rectified, is an oily liquid, green by transmitted, blue by reflected light, and having an intolerably pungent and suffocating odour. It is isomeric with benzonitril, and is resolved by boiling with dilute acids into formic acid and aniline:

$$C_7H_5N + 2H_2O = CH_2O_2 + C_6H_7N.$$

It is a remarkable fact that, whereas the normal alcoholic cyanides are easily decomposed by boiling alkaline solutions, the isocyanides are scarcely altered by alkalis, but are easily hydrated under the influence of acids.

The isocyanides of ethyl and amyl have been obtained by similar processes; namely, by distilling methylamine and ethylamine respectively with chloroform, also by the action of ethylic and amylic iodides on silver cyanide. They resemble the phenyl compound in their reactions, and are also characterised by extremely powerful odours. The repulsive odour possessed by the normal alcoholic cyanides when prepared by distilling potassium cyanide with the ethyl-sulphates or homologous salts, appears to be due to the presence of small quantities of these isocyanides.

The difference of constitution between the normal cyanides and the isocyanides may be represented by the following formulæ, taking the methyl compounds for example:

$$\underset{\text{Cyanide.}}{N\equiv C{-}CH_3 \text{ or } C^{iv}\begin{cases} N''' \\ CH_3 \end{cases}} \qquad \underset{\text{Isocyanide.}}{C\equiv N{-}CH_3 \text{ or } N^{v}\begin{cases} C^{iv} \\ CH_3 \end{cases}}$$

In the isocyanide the carbon belonging to the alcohol-radicle is united directly with the nitrogen; in the cyanide, only through the medium of the carbon belonging to the cyanogen.

This difference of structure may perhaps account for the difference in the reactions of the cyanides and isocyanides, under the influence of hydrating agents, thus:

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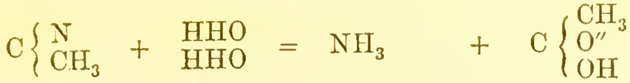
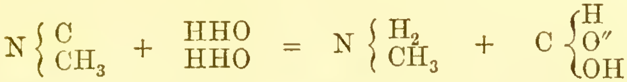
* Proceedings of the Royal Society, xvi. 144, 148, 150.



$$C\left\{\begin{matrix}N\\CH_3\end{matrix}\right. + \begin{matrix}HHO\\HHO\end{matrix} = NH_3 + C\left\{\begin{matrix}CH_3\\O''\\OH\end{matrix}\right.$$

Methyl cyanide. Water (2 mol.) Ammonia. Acetic acid.



$$N\left\{\begin{matrix}C\\CH_3\end{matrix}\right. + \begin{matrix}HHO\\HHO\end{matrix} = N\left\{\begin{matrix}H_2\\CH_3\end{matrix}\right. + C\left\{\begin{matrix}H\\O''\\OH\end{matrix}\right.$$

Methyl isocyanide. Water (2 mol.) Methylamine. Formic acid.

The isocyanides of methyl and ethyl (methyl- and ethyl-carbamines) unite with acids, forming crystallisable salts.

OXYGEN- AND SULPHUR-COMPOUNDS OF CYANOGEN.

Cyanic Acid, CHNO.—Of this acid there are two possible modifications represented by the formulæ:

$$N{\equiv}C{-}OH \text{ and } CO{=}N{-}H\,.$$

These modifications are actually exhibited in the metallic cyanates and the cyanic ethers; but the acid itself is known in one modification only, the particular constitution of which has not yet been determined. It is produced when cyanuric acid, deprived of its water of crystallisation, is heated to dull redness in a hard glass retort connected with a receiver cooled by ice. The cyanuric acid is resolved, without any other product, into cyanic acid, which condenses in the receiver to a limpid, colourless liquid, of exceedingly pungent and penetrating odour, like that of the strongest acetic acid: it even blisters the skin. When mixed with water it decomposes almost immediately, giving rise to ammonium bicarbonate:

$$CHNO + H_2O = CO_2 + NH_3.$$

In consequence of this decomposition, cyanic acid cannot be separated from a cyanate by a stronger acid. A trace of it, however, always escapes decomposition, and communicates to the carbon dioxide evolved a pungent smell similar to that of sulphurous acid. The cyanates may be easily distinguished by this smell, and by the simultaneous formation of an ammonia-salt, which remains behind.

Pure cyanic acid cannot be preserved: shortly after its preparation it changes spontaneously, with sudden rise of temperature, into a solid, white, opaque, amorphous substance, called *cyamelide*. This body has the same composition as cyanic acid: it is insoluble in water, alcohol, ether, and dilute acids: it dissolves in strong oil of vitriol by the aid of heat, with evolution of carbon dioxide and production of ammonia; boiled with a solution of caustic alkali, it dissolves, ammonia being disengaged, and a mixture of cyanate and cyanurate of the base generated. By dry distillation it is reconverted into cyanic acid.

Potassium Cyanate, CNKO.—Of this salt there are two modifications, viz.,

$$\underset{\text{Normal cyanate.}}{N{\equiv}C{-}OK} \quad \text{and} \quad \underset{\text{Isocyanate.}}{CO{=}NK}$$

The normal cyanate, formed by passing gaseous cyanogen chloride (p. 101) into cold aqueous potash, crystallises in long needles, and is converted by fusion into the isocyanate.

The isocyanate (ordinary potassium cyanate) is best prepared by oxidising potassium cyanide with litharge. The cyanide, already containing a portion of cyanate, described at page 83, is remelted in an earthen crucible, and finely powdered lead oxide added by small portions; the oxide is instantaneously reduced, and the metal, at first in a state of minute division, ultimately collects to a fused globule at the bottom of the crucible. The salt is poured out, and, when cold, powdered and boiled with alcohol; the hot filtered solution deposits crystals of potassium isocyanate on cooling. The great deoxidising power exerted by potassium cyanide at a high temperature renders it a valuable agent in many of the finer metallurgic operations.

Another method of preparing the isocyanate is to mix dried and finely powdered potassium ferrocyanide with half its weight of equally dry manganese dioxide; heat this mixture in a shallow iron ladle, with free exposure to air and frequent stirring, until the tinder-like combustion is at an end; and boil the residue in alcohol, which extracts the isocyanate.

The salt crystallises from alcohol in thin, colourless, transparent plates, which suffer no change in dry air, but on exposure to moisture are gradually converted, without much alteration of appearance, into potassium bicarbonate, ammonia being at the same time given off. Water dissolves potassium isocyanate in large quantity; the solution is slowly decomposed in the cold, and rapidly at a boiling heat, into potassium bicarbonate and ammonia. When a concentrated solution is mixed with a small quantity of dilute mineral acid, a precipitate falls, consisting of acid potassium cyanurate. Potassium isocyanate is reduced to cyanide by ignition with charcoal in a covered crucible. Mixed with solutions of lead and silver, it gives rise to white insoluble isocyanates of those metals.

Ammonium Cyanate (probably *iso*), CN_2H_4O, or NH_4CNO.—When the vapour of cyanic acid is mixed with excess of ammoniacal gas, a white, crystalline, solid substance is produced, which has all the characters of a true, although not neutral ammonium cyanate. It dissolves in water, and if mixed with an acid, evolves carbon dioxide: with an alkali, it yields ammonia. But if the solution be heated, or if the crystals be merely exposed for a certain time to the air, a portion of ammonia is dissipated, and the properties of the compound are completely changed. It may now be mixed with acids without the least sign of decomposition, and does not evolve the smallest trace of ammonia when treated with cold caustic alkali

The result of this transformation, as already observed (p. 1), is urea.

Cyanuric Acid, $C_3N_3H_3O_3$.—This substance may be prepared by heating dry and pure urea in a flask or retort: the urea melts, boils, gives off ammonia in large quantity, and at length becomes converted into a dirty-white, solid, amorphous mass, which is impure cyanuric acid. This is dissolved by the aid of heat in strong oil of vitriol, and nitric acid added by small portions till the liquid becomes nearly colourless; it is then mixed with water, and left to cool, whereupon the cyanuric acid separates. The urea may likewise be decomposed very conveniently by gently heating it in a tube, while dry chlorine or hydrochloric acid gas passes over it. A mixture of cyanuric acid and sal-ammoniac results, which is separated by dissolving the latter in water. The reaction with chlorine is represented by the equation:

$$3CON_2H_4 + Cl_3 = C_3N_3H_3O_3 + 2NH_4Cl + HCl + N.$$

Cyanuric acid forms colourless efflorescent crystals, seldom of large size, derived from an oblique rhombic prism. It is very little soluble in cold water, and requires 24 parts for solution at a boiling heat: it reddens litmus feebly, has no odour, and but little taste. The acid is tribasic: the crystals contain $C_3N_3H_3O_3.2\,aq.$, and are easily deprived of their water of crystallisation. In point of stability, cyanuric acid offers a most remarkable contrast to its isomeride, cyanic acid; it dissolves, as above indicated, in hot oil of vitriol, and even in strong nitric acid, without decomposition, and, in fact, crystallises from the latter in the anhydrous state. Long-continued boiling with these powerful agents resolves it into ammonia and carbonic acid.

The connection between cyanic acid, urea, and cyanuric acid, may be thus recapitulated:

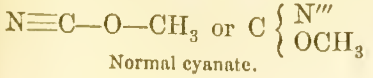
Ammonium cyanate is converted by heat into urea.

Urea is decomposed by the same means into cyanuric acid and ammonia.

Cyanuric acid is changed by a very high temperature into cyanic acid, one molecule of cyanuric acid splitting into three molecules of cyanic acid.

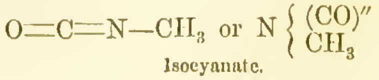
Cyanic and Cyanuric Ethers.

Of each of these ethers there are two series, analogous to the alcoholic cyanides and isocyanides. The difference of their structure is exhibited by the following formulæ, taking the methyl-compounds as examples:



$$N\equiv C-O-CH_3 \text{ or } C\left\{\begin{matrix}N'''\\OCH_3\end{matrix}\right.$$

Normal cyanate.



$$O=C=N-CH_3 \text{ or } N\left\{\begin{matrix}(CO)''\\CH_3\end{matrix}\right.$$

Isocyanate.

The corresponding cyanuric ethers are represented by the formulæ,

$$C_3\left\{\begin{matrix}N_3\\ OCH_3)_3\end{matrix}\right. \text{ and } N_3\left\{\begin{matrix}(CO)_3\\ (CH_3)_3\end{matrix}\right. .$$

The normal cyanic ethers, discovered by Cloez, and the normal cyanuric ethers, discovered by Hofmann,* are produced simultaneously by the action of gaseous cyanogen chloride on the sodium-alcohols: normal ethyl cyanate, for example, from cyanogen chloride and sodium ethylate; thus:

$$C\left\{\begin{matrix}N\\ Cl\end{matrix}\right. + NaOC_2H_5 = NaCl + C\left\{\begin{matrix}N\\ OC_2H_5\end{matrix}\right. .$$

They are decomposed by water, assisted by acids or bases, into cyanic or cyanuric acid and an alcohol: *e.g.*:

$$C\left\{\begin{matrix}N\\ OC_2H_5\end{matrix}\right. + HOH = HOC_2H_5 + C\left\{\begin{matrix}N\\ OH\end{matrix}\right. .$$

The cyanates of methyl, ethyl, and amyl are colourless, oily liquids, decomposed by heat into a volatile portion and a solid residue. The corresponding cyanurates are crystalline solids.

The isocyanic and isocyanuric ethers, or alcoholic carbimides, are produced simultaneously by distilling a dry mixture of potassium isocyanate and methylsulphate, ethylsulphate, &c., *e.g.*:

$$N\left\{\begin{matrix}(CO)\\ K\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ K\end{matrix}\right\}SO_4 = K_2SO_4 + N\left\{\begin{matrix}(CO)\\ C_2H_5\end{matrix}\right. .$$

Ethylic isocyanate and isocyanurate thus obtained are easily separated by distillation, the former boiling at 60°, the latter at 276°. The former is a mobile liquid, the latter a crystalline solid, melting at 85°. The isocyanurate may likewise be obtained by distilling a mixture of potassium cyanurate and ethylsulphate.

The ethers of this class, when heated with a strong solution of caustic alkali, are resolved into carbon dioxide and an alcoholic ammonia or amine, *e.g.*:

$$N\left\{\begin{matrix}(CO)\\ CH_3\end{matrix}\right. + H_2O = CO_2 + N\left\{\begin{matrix}H_2\\ CH_3\end{matrix}\right.$$

Methyl isocyanate. Methylamine.

Fulminic Acid, $C_2N_2H_2O_2$.—This compound, polymeric with cyanic and cyanuric acids, is one of the products formed by the action of nitrous acid upon alcohol in presence of a salt of silver or mercury. The acid itself, or hydrogen fulminate, has not been obtained.

Silver fulminate is prepared by dissolving 40 or 50 grains of silver, which need not be pure, in about ¾ oz. by measure of nitric acid of sp. gr. 1·37, with the aid of a little heat. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat is applied until reaction commences. The nitric acid oxidises part of the alcohol to aldehyde and oxalic acid, becoming itself reduced to nitrous acid, which, in turn, acts upon the alcohol in such a manner as to form nitrous ether, fulminic acid, and water, 1 molecule of nitrous ether and 1 molecule of nitrous acid containing the elements of 1 molecule of fulminic acid and 2 molecules of water:

---

* The isocyanic and isocyanuric ethers having been discovered first (by Wurtz in 1848), were originally called cyanic and cyanuric ethers.

$$C_2H_5NO_2 + HNO_2 = C_2N_2H_2O_2 + 2H_2O\,.$$

The silver fulminate slowly separates from the hot liquid, in the form of small, brilliant, white, crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter-paper in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box. The only perfectly safe method of keeping the salt is by immersing it in water. Silver fulminate is soluble in 36 parts of boiling water, but the greater part crystallises out on cooling: it is one of the most dangerous substances known, exploding with fearful violence when strongly heated, or when rubbed or struck with a hard body, or when touched with concentrated sulphuric acid: the metal is reduced, and a large volume of gaseous matter suddenly liberated. Nevertheless, when very cautiously mixed with copper oxide, it may be burned in a tube with as much facility as any other organic substance. Its composition thus determined is expressed by the formula $Ag_2C_2N_2O_2$.

Fulminic acid is bibasic: when silver fulminate is digested with caustic potash, one-half of the silver is precipitated as oxide, and a *silver-potassium fulminate*, $AgKC_2N_2O_2$, is produced, which resembles the neutral silver-salt, and detonates by a blow. Corresponding compounds containing sodium or ammonium exist; but a pure fulminate of an alkali-metal has never been formed. If silver fulminate be digested with water and copper, or zinc, the silver is entirely displaced, and a fulminate of the other metal produced. The zinc-salt mixed with baryta-water gives rise to a precipitate of zinc oxide, while *zinco-baric fulminate*, $ZnBa(C_2N_2O_2)_2$, remains in solution.—*Mercuric fulminate*, $HgC_2N_2O_2$, is prepared by a process very similar to that by which the silver-salt is obtained. One part of mercury is dissolved in 12 parts of nitric acid; the solution is mixed with an equal quantity of alcohol; and gentle heat is applied, the reaction, if too violent, being moderated by adding more spirit from time to time. Much carbonic acid, nitrogen, and red vapours are disengaged, together with a large quantity of nitrous ether and aldehyde: these are sometimes condensed and collected for sale, but are said to contain hydrocyanic acid. The mercuric fulminate separates from the hot liquid, and after cooling may be purified from an admixture of reduced metal by solution in boiling water and re-crystallisation. It much resembles the silver-salt in appearance, properties, and degree of solubility. It explodes violently by friction or percussion, but unlike the silver-compound, merely burns with a sudden and almost noiseless flash when kindled in the open air. It is manufactured on a large scale for the purpose of charging *percussion-caps;* sulphur and potassium chlorate, or more frequently nitre, are added, and the powder, pressed into the cap, is secured by a drop of varnish.

The relation of composition between the three isomeric acids is shown by comparison of their silver-salts : the first acid is monobasic, the second bibasic, and the third tribasic :

Silver cyanate,	$Ag\,C\,N\,O$
Silver fulminate,	$Ag_2C_2N_2O_2$
Silver cyanurate,	$Ag_3C_3N_3O_3$.

Fulminic, as well as cyanic acid, may be converted into urea. Dr. Gladstone has shown that, when a solution of copper fulminate is mixed with excess of ammonia, filtered, treated with sulphuretted hydrogen in excess, and again filtered from the insoluble copper sulphide, the liquid obtained is a mixed solution of urea and ammonium thiocyanate.

Another view regarding the constitution of fulminic acid was proposed by Gerhardt. The fulminates may be considered as methyl cyanide (acetonitril), in which one atom of hydrogen is replaced by NO_2 and 2 atoms of hydrogen by mercury or silver :

$C\ H\ \ H\,H\,CN$	Methyl cyanide.
$C(NO_2)AgAgCN$	Silver fulminate.
$C(NO_2)\ Hg''CN$	Mercuric fulminate.

This view has received some support by the interesting observation, made by Kekulé, that the action of chlorine upon mercuric fulminate gives rise to the formation of chloropicrin, $C(NO_2)Cl_3$ (p. 80). The connection of fulminic acid with the methyl series is thus established.

Fulminuric Acid, $C_3N_3H_3O_3$.—This acid, isomeric with cyanuric acid, was discovered simultaneously by Liebig and by Schischkoff. It is obtained by the action of a soluble chloride upon mercuric fulminate. On boiling mercuric fulminate with an aqueous solution of potassium chloride, the mercury salt gradually dissolves, and the clear solution, after some time, becomes turbid, in consequence of a separation of mercuric oxide ; it then contains potassium fulminurate :

$$3HgC_2N_2O_2 + 8KCl + H_2O = 4KCl + 2HgCl_2 + HgO + 2C_3N_3HK_2O_3.$$

If, instead of potassium chloride, sodium or ammonium chloride be employed, the corresponding sodium and ammonium-compounds are obtained. The fulminurates crystallise with great facility : they are not explosive.

Fulminuric acid has the same composition as cyanuric acid, but it is bibasic, whereas cyanuric acid is tribasic.

Cyanogen Chlorides.—Chlorine forms with cyanogen, or its elements, two compounds, which are polymeric, and analogous to cyanic and cyanuric acids. *Gaseous cyanogen chloride*, CyCl, is formed by passing chlorine gas into anhydrous hydrocyanic acid, or by passing chlorine over moist mercuric cyanide contained in a tube sheltered from the light. It is a permanent and colourless gas at the temperature of the air, of insupportable pungency, and soluble to a very considerable extent in water, alcohol, and ether. At $-18°$ it congeals to a mass of colourless crystals, which at $-15°$ melt to a liquid whose boiling point is $-11·6°$. At the temperature of the air it is condensed to the liquid form under a pressure of four atmospheres, and when long preserved in this state in hermetically sealed tubes, gradually passes into the solid modification.

On passing gaseous cyanogen chloride into a solution of ammonia in anhydrous ether, cyanamide, CN_2H_2, is formed together with sal-ammoniac.

Solid cyanogen chloride, $C_3N_3Cl_3$, or Cy_3Cl_3, is generated when anhydrous hydrocyanic acid is put into a vessel of chlorine gas, and the whole exposed to the sun: hydrochloric acid is formed at the same time. It forms long colourless needles, which exhale a powerful and offensive odour, compared by some to that of the excrement of mice ; it melts at 140°, and sublimes unchanged at a higher temperature. When heated in contact with water, it is decomposed into cyanuric and hydrochloric acid. It dissolves in alcohol and ether without decomposition.

Cyanogen Bromide and *Iodide* correspond with the first of the preceding compounds, and are prepared by distilling bromine or iodine with mercuric cyanide. They are colourless, volatile, solid substances, of powerful odour.

Cyanogen Sulphide, C_2N_2S, or Cy_2S, recently obtained by Linnemann by the action of cyanogen iodide upon silver thiocyanate, crystallises in transparent, volatile, rhombic plates, having an odour similar to that of cyanogen iodide. It melts at 60°, but decomposes rapidly at a higher temperature ; dissolves in ether, alcohol, and water, and separates from hot concentrated solutions, on cooling, in the crystalline form.

Thiocyanic Acid, CNHS, also called *Sulphocyanic acid.*—This acid is the sulphur analogue of cyanic acid, and, like the latter, is monobasic, the thiocyanates of monad metals being represented by the formula MCNS.

Potassium Thiocyanate, CNKS.—To prepare this salt, yellow potassium ferrocyanide, deprived of its water of crystallisation, is intimately mixed with half its weight of sulphur, and the whole heated to tranquil fusion in an iron pot, and kept for some time in that condition. When cold, the melted mass is boiled with water, which dissolves out a mixture of potassium thiocyanate and iron thiocyanate, leaving little behind but the excess of sulphur. This solution, which becomes red on exposure to the air, from oxidation of the iron, is mixed with potassium carbonate, by which the iron is precipitated, and potassium substituted: an excess of the carbonate must be, as far as possible, avoided. The filtered liquid is concentrated, by evaporation over an open fire, to a small bulk, and left to cool and crystallise. The crystals are drained, purified by re-solution, if necessary, or dried by enclosing them, spread on filter-paper, over a surface of oil of vitriol covered with a bell-jar.

The reaction between the sulphur and the potassium ferrocyanide is represented by the equation:

$$K_4FeC_6N_6 + S_6 = 4KCNS + Fe(CNS)_2.$$

Another, and even better process, consists in gradually heating to low redness in a covered vessel a mixture of 46 parts of dried potassium ferrocyanide, 32 of sulphur, and 17 of pure potassium carbonate. The mass is exhausted with water, the aqueous solution is evaporated to dryness, and the residue is exhausted with alcohol. The alcoholic liquid deposits splendid crystals on cooling or evaporation.

Potassium thiocyanate crystallises in long, slender, colourless prisms, or plates, which are anhydrous: it has a bitter saline taste, and is destitute of poisonous properties: it is very soluble in water and alcohol, and deliquesces when exposed to a moist atmosphere. When heated, it melts to a colourless liquid, at a temperature far below that of ignition.

Chlorine, passed into a strong solution of potassium thiocyanate, throws down a large quantity of a bulky, deep yellow, insoluble substance, formerly called sulphocyanogen, from its supposed identity with the radicle of the sulphocyanates: it is, however, invariably found to contain hydrogen, and is represented by the formula $C_3N_3HS_3$. This yellow substance, now generally called persulphocyanogen, is quite insoluble in water, alcohol, and ether. When heated in the dry state, it evolves sulphur and carbon bisulphide, and leaves a pale, straw-yellow substance, called hydromellone, $C_6N_9H_3$, the decomposition being represented by the equation:

$$3C_3N_3HS_3 = 3CS_2 + S_3 + C_6N_9H_3.$$

Hydrogen Thiocyanate, or *Thiocyanic Acid*, HCNS, is obtained by decomposing lead thiocyanate, suspended in water, with sulphuretted hydrogen. The filtered solution is colourless, very acid, and not poisonous: it is easily decomposed, in a very complex manner, by ebullition, and by exposure to the air. By neutralising the liquid with ammonia, and evaporating very gently to dryness, *ammonium thiocyanate*, NH_4CNS, is obtained as a deliquescent, saline mass. The salt may be conveniently prepared by digesting hydrocyanic acid with yellow ammonium sulphide (containing excess of sulphur), and boiling off the excess of the latter:

$$2HCN + (NH_4)_2S + S_2 = H_2S + 2(NH_4)CNS.$$

The thiocyanates of *sodium, barium, strontium, calcium, manganese,* and *ferrous thiocyanate*, are colourless and very soluble; those of *lead* and *silver* are white and insoluble. A soluble thiocyanate mixed with a ferric salt gives no precipitate, but causes the liquid to assume a blood-red tint: hence the use of potassium thiocyanate as a test for iron in the state of ferric salt. The red colour produced by thiocyanates in ferric solutions is exactly like that caused under similar circumstances by meconic acid. The two substances may, however, be readily distinguished by the addition of a solution of gold chloride, which destroys the colour produced by thiocyanates. The ferric meconate may also be distinguished from the thiocyanate by an addition of corrosive sublimate, which bleaches the thiocyanate, but has little effect upon the meconate. This is a point of considerable practical importance, as in medico-legal inquiries, in which evidence of the presence of opium is sought for in complex organic mixtures, the detection of meconic acid is usually the object of the chemist; and since traces of alkaline thiocyanate are to be found in the saliva, it becomes very desirable to remove that source of error and ambiguity.

The great facility with which hydrocyanic acid may be converted into ammonium thiocyanate enables us to ascertain its presence by the iron test just described. The cyanide to be examined is mixed in a watch-glass with some hydrochloric acid and covered with another watch-glass, to which a few drops of yellow ammonium sulphide adhere. On heating the mixture, hydrocyanic acid is disengaged, which combines with the ammonium sulphide, and produces ammonium thiocyanate: this, after expulsion of the excess of sulphide, yields the red colour with solution of ferric chloride.

Thiocyanic Ethers.—These ethers exhibit isomeric modifications analogous to those of the alcoholic cyanates and isocyanates (p. 97). The normal thiocyanates of methyl and its homologues were discovered by Cahours; and Hofmann has obtained the corresponding isothiocyanates. The same chemist some years ago obtained phenyl isothiocyanate. Allyl thiocyanate has long been known as a natural product.

Normal Ethyl Thiocyanate, $C\left\{\begin{matrix}N\\S_2CH_5\end{matrix}\right.$, is obtained by saturating a concentrated solution of potassium thiocyanate with ethyl chloride:

$$C\left\{\begin{matrix}N\\SK\end{matrix}\right. + C_2H_5Cl = KCl + C\left\{\begin{matrix}N\\SC_2H_5\end{matrix}\right.;$$

also by distilling a mixture of calcium ethylsulphate and potassium thiocyanate. It is a mobile, colourless, strongly refracting liquid, having a somewhat pungent odour like that of mercaptan. It boils at 146°. With ammonia it does not combine directly, but yields products of decomposition.

The methyl and amyl thiocyanic ethers resemble the ethyl compound, and are obtained by similar processes. The methyl ether boils at about 132°; the amyl ether at 197°.

Ethyl Isothiocyanate, or *Ethylic Thiocarbimide,* $N\left\{\begin{matrix}(CS)''\\C_2H_5\end{matrix}\right.$, is produced by distilling diethyl-thiocarbamide with phosphoric oxide, which abstracts ethylamine:

$$N_2\left\{\begin{matrix}(CS)''\\(C_2H_5)_2\\H_2\end{matrix}\right. \quad - \quad N\left\{\begin{matrix}C_2H_5\\H_2\end{matrix}\right. \quad = \quad N\left\{\begin{matrix}(CS)''\\C_2H_5\end{matrix}\right.$$

Diethyl-thiocarbamide. Ethylamine. Ethyl-isothiocyanate.

This ether differs essentially in all its properties from ethyl thiocyanate. It boils at 134°, and has a powerfully irritating odour, like that of mustard-oil, and quite different from that of normal ethyl sulphocyanate. It unites directly with ammonia in alcoholic solution, forming ethylthiocarbamide, $N_2(CS)''(C_2H_5)H_3$, and forms similar compounds with methylamine and ethylamine. The pungent odour, and the direct combination with ammonia and amines, are characteristic of all the ethers of this group.

Phenyl Isothiocyanate, $N(CS)''(C_6H_5)$, is obtained by distilling phenysulphocarbamide, $N_2(CS)''(C_6H_5)H_3$, with phosphoric oxide; *naphthyl isothiocyanate,* $N(CS)''(C_{10}H_7)$, in like manner from dinaphthylsulphocarbamide. The former boils at 220°.

Allyl Isothiocyanate, or *Allylic Thiocarbimide,* $N\left\{\begin{matrix}(CS)''\\C_3H_5\end{matrix}\right.$.—This is the intensely pungent volatile oil obtained by distilling the seeds of black mustard with water. It does not exist ready-formed in the seeds, but is produced by the decomposition of myronic acid under the influence of myrosin, an albuminous substance analogous to the synaptase of bitter almonds. The same compound, or perhaps its isomeride, normal allyl thiocyanate, is produced by the action of potassium thiocyanate or silver thiocyanate on allyl iodide or allyl oxide.

Oil of mustard is a transparent, colourless, strongly refracting oil, possessing in the highest degree the sharp penetrating odour of black mustard. The smallest quantity of the vapour excites tears, and is apt to produce inflammation of the eyes. It has a burning taste, and rapidly blisters the skin. Its specific gravity is 1·009 at 15°. It boils at 148°. It is sparingly soluble in water, easily soluble in alcohol and ether; dissolves sulphur and phosphorus when heated, and deposits them in the crystalline state on cooling. It is violently oxidised by nitric and by nitromuriatic acid. Heated in a sealed tube with potassium monosulphide, it yields potassium thiocyanate and allyl sulphide (volatile oil of garlic).

$$2(C_3H_5)NCS + K_2S = 2KCNS + (C_3H_5)_2S.$$

It likewise yields garlic oil when decomposed by potassium. Heated to 120° in a sealed tube with pulverised soda-lime, it yields sodium thiocyanate and allyl oxide, the oxidised constituent of garlic oil:

$$2(C_3H_5)NCS + Na_2O = 2NaCNS + (C_3H_5)_2O.$$

Aqueous potash, soda, baryta, and the oxides of lead, silver, and mercury, in presence of water, convert oil of mustard into sinapoline, $C_7H_{12}N_2O$, with formation of metallic sulphide and carbonate; thus:

$$2(C_3H_5)NCS + 3PbO + H_2O = 2PbS + PbCO_3 + C_7H_{12}N_2O.$$

Sinapoline is a basic substance, which crystallises in colourless plates, soluble in water and alcohol, and having a distinct alkaline reaction.

Oil of mustard readily unites with ammonia, forming thiosinamine, $C_4H_5NS \, . \, NH_3$, or allyl-thiocarbamide, $N_2\left\{\begin{matrix}(CS)''\\ C_3H_5\\ H_3\end{matrix}\right.$; which is also a basic compound, forming colourless prismatic crystals, having a bitter taste, and soluble in water. The solution does not affect test-paper. Thiosinamine melts when heated, but cannot be sublimed. Acids combine with it, but do not form crystallisable salts; the double salts of the hydrochloride with platinic and mercuric chlorides are the most definite.

Thiosinamine is decomposed by metallic oxides, as lead oxide or mercuric oxide, with production of a metallic sulphide and sinamine, $C_4H_6N_2$, a basic compound which crystallises very slowly from a concentrated aqueous solution, in brilliant, colourless crystals containing water. It has a powerfully bitter taste, is strongly alkaline to test-paper, and decomposes ammonium-salts at the boiling heat. Its oxalate is crystallisable. The formation of sinamine from thiosinamine by the action of mercuric oxide is represented by the equation, $C_4H_8N_2S + HgO = HgS + H_2O + C_4H_6N_2$.

Seleniocyanates.—A series of salts containing selenium, and corresponding in composition and properties with the thiocyanates, have been discovered and examined by Mr. Crookes.*

AMIDO-DERIVATIVES OF CYANIC AND CYANURIC ACIDS.

Cyanamide, $CN.NH_2$, is formed by the action of chloride or bromide of cyanogen on ammonia dissolved in ether:

$$CNCl + NH_3 = HCl + CN.NH_2,$$

also by the action of carbon dioxide on sodamide, NH_2Na:

$$CO_2 + 2NH_2Na = 2NaOH + CN.NH_2,$$

and by desulphurising thiocarbamide with oxide of lead or mercury:

$$CS(NH_2)_2 + O = CN_2H_2 + H_2O + S.$$

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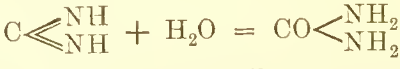
* Journal of the Chemical Society, iv. 12.

Cyanamide forms colourless crystals, easily soluble in water, alcohol, and ether, melting at 40°. The solutions give with ammoniacal silver nitrate a yellow precipitate of argentocyanamide, CN_2Ag_2, and with cupric sulphate a black precipitate of cuprocyanamide, CN_2Cu. By nitric, sulphuric or phosphoric acid cyanamide is converted into carbamide, $CO(NH_2)_2$. In this and most of its reactions it behaves as if it had the structure of carbodiimide, $\mathrm{C}{\lessdot}\begin{matrix}\mathrm{NH}\\\mathrm{HH}\end{matrix}$; thus:



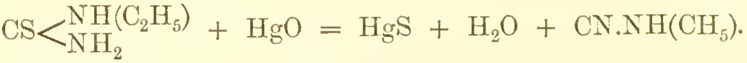
$$\mathrm{C}{\lessdot}\begin{matrix}\mathrm{NH}\\\mathrm{NH}\end{matrix} + H_2O = \mathrm{CO}{<}\begin{matrix}\mathrm{NH_2}\\\mathrm{NH_2}\end{matrix}.$$

Hydrogen sulphide converts it, in like manner, into thiocarbamide, $CS(NH_2)_2$.

Alcoholic derivatives of cyanamide are formed by the action of cyanogen chloride on primary amines dissolved in ether:

$$\underset{\text{Ethylamine.}}{C_2H_5.NH_2} + CNCl = HCl + \underset{\text{Ethylcyanamide.}}{CN.NH(C_2H_5)};$$

also by heating the corresponding thiocarbamides with mercuric oxide and water:



$$\mathrm{CS}{<}\begin{matrix}\mathrm{NH(C_2H_5)}\\\mathrm{NH_2}\end{matrix} + HgO = HgS + H_2O + CN.NH(CH_5).$$

Methyl-cyanamide and *Ethyl-cyanamide* are thick uncrystallisable syrups, having a neutral reaction, and easily converted into polymeric modifications.

Allyl-cyanamide, $CN.NH(C_3H_5)$, prepared from allyl-thiocarbamide, easily changes into the polymeric compound, triallymelamine, $C_3N_6H_3(C_3H_5)_3$.

Dicyanimide, $NH(CN)_2$, is formed by the action of potash on normal potassium cyanate (p. 96):

$$3(CN.OK) + KOH = NH(CN)_2 + CO_3K_2 + K_2O.$$

Dicyanodiamide, $C_2N_4H_4 = C_2N_2(NH_2)_2$ (*Param*) is formed, by polymerisation of cyanamide, when the aqueous solution of the latter is left to itself, or evaporated; also when thiocarbamide is boiled with mercuric oxide or silver oxide. It is easily soluble in water and in alcohol, and crystallises in rhombic plates, melting at 205°. On adding silver nitrate to its aqueous solution, the compound $C_2N_4H_3Ag + NO_3H$ crystallises out in silky needles.

Cyanuramides.—From cyanuric acid, $C_3N_3(OH)_3$, may be derived three amides, viz.:

$$\underset{\text{Ammelide.}}{C_3N_3\left\{\begin{matrix}(OH)_2\\NH_2\end{matrix}\right.} \qquad \underset{\text{Ammeline.}}{C_3N_3\left\{\begin{matrix}OH\\(NH_2)_2\end{matrix}\right.} \qquad \underset{\text{Melamine.}}{C_3N_3(NH_2)_3}$$

Melamine or *Cyanuramide*, $C_3N_6H_6 = N_3\left\{\begin{matrix}(C_3N_3)\\H_6\end{matrix}\right.$, is formed by polymerisation of cyanamide when the latter is heated to 150°; it is, however, more easily prepared by heating melam with potash-ley, the melam being then resolved into melamine and ammeline.

Melamine crystallises in shining rhombic octohedrons, easily soluble in water, but insoluble in alcohol and ether, It forms well-crystallised salts containing 1 equivalent of acid, *e.g.*, $C_3N_6H_6.HCl$. When boiled with acids or alkalis, it is converted successively, by assumption of H_2O and elimination of NH_3, into ammeline, ammelide, and cyanuric acid.

Triethyl- and *trimethyl-melamine* are formed by polymerisation of ethyl- and methyl-cyanamide, when the aqueous solutions of those bodies are evaporated. They are crystalline, strongly alkaline bodies, which are converted, by boiling with hydrochloric acid, into the corresponding derivatives of ammeline, and ultimately into isocyanuric ethers.

Ammeline, $C_3N_5H_5O = C_3N_3\left\{\begin{matrix}OH\\(NH_2)_2\end{matrix}\right.$, is a white powder insoluble in water, alcohol, and ether, but soluble in acids and alkalis, and forming crystalline salts, which are decomposed by water.

Ammelide, $C_3N_4H_4O_2 = C_3N_3\left\{\begin{matrix}(OH)_2\\(NH)_2\end{matrix}\right.$, is a white powder which dissolves in alkalis and in concentrated acids, but does not form definite salts with the latter. Its ammoniacal solution gives with silver nitrate a white precipitate having the composition

$$C_3N_3\left\{\begin{matrix}OH\\OAg\\NH_2\end{matrix}\right. .$$

Melam, $C_6H_9N_{11}$, is a buff-coloured, insoluble, amorphous substance, obtained by the distillation of ammonium thiocyanate at a high temperature. It may be prepared in large quantity by intimately mixing 1 part of perfectly dry potassium thiocyanate with 2 parts of powdered sal-ammoniac, and heating the mixture for some time in a retort or flask: carbon bisulphide, ammonium sulphide, and sulphuretted hydrogen, are disengaged and volatilised, while a mixture of melam, potassium chloride, and sal-ammoniac remains; the two latter substances are removed by washing with hot water. Melam dissolves in concentrated sulphuric acid, and gives, by dilution with water and long boiling, cyanuric acid. The same substance is produced, with disengagement of ammonia, when melam is fused with potassium hydrate. When strongly heated, melam is resolved into mellone and ammonia:

$$3C_6N_{11}H_9 = 2C_9N_{12} + 9NH_3 ;$$

and by prolonged boiling with moderately strong caustic potash, it is resolved into melamine and ammeline:

$$C_6N_{11}H_9 + H_2O = C_3N_6H_6 + C_3N_5H_5O$$

Mellone and Mellonides.—The name mellone was given by Liebig to a yellow insoluble substance obtained as a residue in the decomposition of perthiocyanogen, or of melam, at a low red heat. The composition of the product thus obtained varies with the duration of the heating. If the decomposition be stopped at a certain point, the product has the composition of dicyanuramide, $N_3\left\{\begin{matrix}(C_3N_3)'''\\(C_3N_3)'''\\H_3\end{matrix}\right.$; but this when further heated still gives off ammonia, and becomes continually richer in carbon, approaching, in fact, continually nearer to the composition of tricyanuramide, $C_9N_{12} = N_3(C_3N_3)_3$, which is probably the ultimate product of the decomposition, though it has never been actually attained, the product always containing a small quantity of hydrogen, however long the heating may be continued.

Mellone is also produced by ignition of ammonium thiocyanate and mercury thiocyanate. When boiled with nitric acid, it is resolved into ammonia and cyanuric acid.

Mellonides, $C_9N_{13}M_3$ (M denoting a monatomic positive radicle).—*Tripotassic mellonide*, $C_9N_{13}K_3$, is produced by ignition of potassium thiocyanate, the preparation being greatly facilitated by the presence of a metallic compound, such as trichloride of antimony or bismuth, capable of taking up a portion of the sulphur which is set free as carbon sulphide. It may also be prepared by fusing potassium thiocyanate with crude mellone, or the ferrocyanide with half its weight of sulphur. The fused mass obtained by either process is dissolved in boiling water, from which the tripotassic mellonide crystallises on cooling in silky needles, containing $C_9N_{13}K_3 + 5H_2O$, insoluble in alcohol and in ether. Acetic acid converts this salt into *dipotassic mellonide*, $C_9N_{13}K_2H$, which is also soluble. Hydrochloric acid produces the *monopotassic salt*, $C_9N_{13}KH_2$, which is insoluble. These three salts stand to each other in the same relation as the several salts of phosphoric and cyanuric acids. Tripotassic mellonide produces, with soluble silver salts, a white precipitate, $C_9N_{13}Ag_3$; with lead salts and mercury salts, precipitates containing respectively $(C_9N_{13})_2Pb_3$ and $(C_9N_{13})_2Hg_3$. The latter, dissolved in hydrocyanic acid and treated with sulphuretted hydrogen, yields *hydromellonic* acid, $C_9N_{13}H_3$, which is known only in solution, has an acid taste, and is decomposed by evaporation into ammonia and mellone.

Cyameluric acid, $C_6N_7O_3H_3$.—The potassium salt of this acid is formed by boiling tripotassic mellonide with strong potash-ley, and the acid itself may be separated from the solution of the salt by a mineral acid in the form of a crystalline precipitate. It is a strong tribasic acid, converted by heating with mineral acids into cyanuric acid.

ALCOHOLS AND ETHERS.

The term alcohol, originally limited to one substance, viz., spirit of wine, is now applied to a large number of organic compounds, many of which, in their external characters, exhibit but little resemblance to common alcohol. They are all, however, analogously constituted, having the composition of hydrocarbons in which one or more of the hydrogen-atoms are replaced by hydroxyl; they may therefore be regarded as compounds of hydroxyl with univalent or multivalent hydrocarbon-radicles, hence called alcohol-radicles. Thus from propane C_3H_8, are derived the three alcohols:

$C_3H_7(OH)$	$C_3H_6(OH)_2$	$C_3H_5(OH)_3$
Propyl alcohol.	Propene alcohol.	Propenyl alcohol.

Alcohols are accordingly classed as monatomic, diatomic, triatomic, &c., or generally as monatomic and polyatomic, according to the number of hydroxyl-groups which they contain, or according to the equivalent values of their hydrocarbon-radicles.

The replacement, partial or total, of the hydroxyl in an alcohol by chlorine, bromine, iodine, or fluorine, gives rise to haloïd ethers; thus:

From $C_3H_7(OH)$ are derived C_3H_7Cl, C_3H_7Br, &c.
„ $C_3H_6(OH)_2$ „ $C_3H_6Cl(OH)$, $C_3H_6Cl_2$, &c.
„ $C_3H_5(OH)_3$ „ $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2(OH)$, $C_3H_5Cl_3$, &c.

These substitutions are effected by treating the alcohols with the chlorides, bromides, and iodides of hydrogen or phosphorus, as in the following equations, which represent the formation of ethyl choride from common alcohol:

$$C_2H_5(OH) + HCl = H(OH) + C_2H_5Cl$$
$$3C_2H_5(OH) + PCl_3 = P(OH)_3 + 3C_2H_5Cl$$
$$3C_2H_5(OH) + POCl_3 = PO(OH)_3 + 3C_2H_5Cl$$

Instead of the bromides and iodides of phosphorus, the elements phosphorus and bromine or iodine, in the proportions required to form them, are often used in these processes.

These haloïd ethers are also formed in many instances by direct substitution of chlorine, bromine, &c., for hydrogen in saturated hydrocarbons, as explained in the preceding pages.

The treatment of the haloïd ethers with caustic aqueous alkalis gives rise to a substitution opposite to that exhibited in the above equations, reconverting the ethers into alcohols, *e.g.*:

$$C_2H_5Cl + KOH = KCl + C_2H_5(OH).$$

A considerable portion of the alcohol thus produced is, however, converted, by dehydration, into the corresponding olefine; *e.g.*: $C_3H_8O - H_2O = C_3H_6$. A better result is obtained by heating the haloïd ether with moist silver oxide, which acts like a hydroxide, AgOH. A still better method is to convert the alcoholic chloride, &c., into an acetate, by heating it with acetate of silver or potassium, and boil the resulting acetic ether with caustic potash or soda; thus:

$$C_2H_5Cl + \underset{\text{Potassium acetate.}}{KC_2H_3O_2} = KBr + \underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2}$$

and

$$\underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2} + KOH = \underset{\text{Ethyl alcohol.}}{C_2H_5OH} + \underset{\text{Potassium acetate.}}{K.C_2H_3O_2}$$

The replacement of the hydroxyl in an alcohol by the corresponding radicles, potassoxyl, OK, methoxyl, OCH_3, ethoxyl, OC_2H_5, &c. (i. 264),—or of the hydrogen in the hydroxyl by potassium, methyl, ethyl, &c.,—gives rise to oxygen-ethers; thus:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5(OH)} \text{ yields } \underset{\text{Potassium ethylate.}}{C_2H_5(OK)} \quad \underset{\text{Methyl ethylate.}}{C_2H_5(OCH_3)} \quad \underset{\text{Ethyl ethylate.}}{C_2H_5(OC_2H_5)}$$

$$\underset{\text{Ethene alcohol.}}{C_2H_4(OH)_2} \quad \text{,,} \quad \underset{\text{Monethylic ethenate.}}{C_2H_4(OH)(OC_2H_5)} \qquad \underset{\text{Diethylic ethenate.}}{C_2H_4(OC_2H_5)_2}$$

These substitutions may be effected in various ways. The simplest is to replace an atom of hydrogen in the alcohol by potassium or sodium, and act on the resulting compound with a haloïd ether; thus:

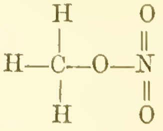
$$\underset{\text{Ethene alcohol.}}{2C_2H_4(OH)_2} + Na_2 = \underset{\text{Sodium ethenate.}}{2C_2H_4(OH)(ONa)} + H_2,$$

$$\underset{\text{Sodium ethenate.}}{C_2H_4(OH)(ONa)} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Sodium iodide.}}{NaI} + \underset{\text{Monethylic ethenate.}}{C_2H_4(OH)(OC_2H_5)}$$

In the polyatomic alcohols, two hydroxyl groups may also be replaced by one atom of oxygen, giving rise to another class of oxygen ethers; thus, from ethene alcohol, $C_2H_4(OH)_2$, is derived ethene oxide, C_2H_4O.

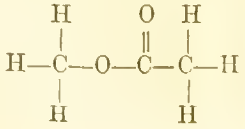
The replacement of the hydrogen of the hydroxyl in an alcohol by acid radicles (p. 26), produces ethereal salts or compound ethers: thus, from methyl alcohol, $CH_3(OH)$, are derived:

Methyl nitrate, $CH_3(ONO_2)$, or

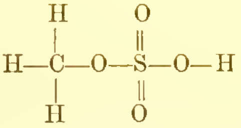


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{N}}$$

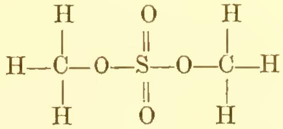
Methyl acetate, $CH_3(OC_2H_3O)$, or



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

Acid methyl sulphate, $CH_3(OSO_3H)$, or 

$$\begin{array}{ccccccccccc} & & H & & & & O & & & & \\ & & | & & & & \| & & & & \\ H & - & C & - & O & - & S & - & O & - & H \\ & & | & & & & \| & & & & \\ & & H & & & & O & & & & \end{array}$$

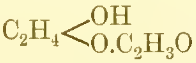
Neutral methyl sulphate, $CH_3(OSO_3CH_3)$, or 

$$\begin{array}{ccccccccccccc} & & H & & & & O & & & & H & & \\ & & | & & & & \| & & & & | & & \\ H & - & C & - & O & - & S & - & O & - & C & - & H \\ & & | & & & & \| & & & & | & & \\ & & H & & & & O & & & & H & & \end{array}$$

These ethereal salts may also be derived from the corresponding acids by substitution of alcohol-radicles for hydrogen, being in fact related to the alcohols in the same manner as metallic salts to metallic hydroxides. When distilled with alkalis, they are resolved into an acid and an alcohol; *e.g.*:

$$\underset{\text{Ethyl acetate.}}{C_2H_5(OC_2H_3O)} + \underset{\text{Potassium hydroxide.}}{K(OH)} = \underset{\text{Potassium acetate.}}{K(OC_2H_3O)} + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)}$$

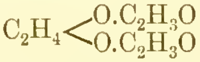
The number of compound ethers that can be formed by a given acid and alcohol depends upon the number of hydroxyl-groups which each of them contains, in other words, on their atomicity: thus, ethyl alcohol, C_2H_5OH, and acetic acid, $C_2H_3O.OH$, both of which are monatomic, yield but one ether, viz., ethyl acetate, $C_2H_3O.O.C_2H_5$; but ethene alcohol or glycol, $C_2H_4.(OH)_2$, which is diatomic, forms two ethers with acetic acid, viz.:



$$C_2H_4\left<\begin{array}{l}OH\\O.C_2H_3O\end{array}\right.$$

Mono-acetate.

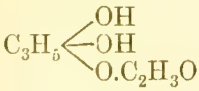
and



$$C_2H_4\left<\begin{array}{l}O.C_2H_3O\\O.C_2H_3O\end{array}\right.$$

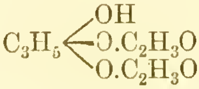
Diacetate.

and glycerin, $C_3H_5(OH)_3$, which is triatomic, forms three acetic ethers, viz.:



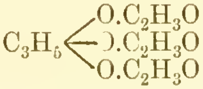
$$C_3H_5\left<\begin{array}{l}OH\\OH\\O.C_2H_3O\end{array}\right.$$

Acetin.



$$C_3H_5\left<\begin{array}{l}OH\\O.C_2H_3O\\O.C_2H_3O\end{array}\right.$$

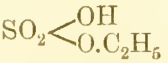
Diacetin.



$$C_3H_5\left<\begin{array}{l}O.C_2H_3O\\O.C_2H_3O\\O.C_2H_3O\end{array}\right.$$

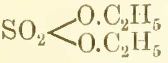
Triacetin.

On the other hand, nitric acid, $NO_2.OH$, which is monatomic, forms but one ethylic ether, viz., ethyl nitrate, $NO_2.O.C_2H_5$; but sulphuric acid, $SO_2(OH)_2$, which is diatomic, forms two ethylic ethers, viz.:



$$SO_2\left<\begin{array}{l}OH\\O.C_2H_5\end{array}\right.$$

Ethyl-sulphuric acid.



$$SO_2\left<\begin{array}{l}O.C_2H_5\\O.C_2H_5\end{array}\right.$$

Diethylic sulphate.

Compound ethers are formed:—1. By the action of the acids upon alcohols; *e.g.*:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5.OH} + \underset{\text{Nitrous acid.}}{NO.OH} = H_2O + \underset{\text{Ethyl nitrite}}{NO.O.C_2H_5}$$

This action takes place slowly at ordinary, more quickly at high temperatures; but the etherification is never complete, as the water separated in the process always exerts a reverse action on the ether, reconverting part of it into alcohol and acid.

Polybasic acids, acting upon alcohols, produce for the most part acid ethers.

2. By the action of chlorides of acid radicles on alcohols or their sodium derivatives:

$$\underset{\text{Sulphuric chloride.}}{SO_2Cl_2} + \underset{\text{Ethyl alcohol.}}{2(C_2H_5O.OH)} = 2HCl + \underset{\text{Ethyl sulphate.}}{SO_2(O.C_2H_5)_2}$$

3. By the action of haloïd ethers on the potassium or silver salts of the corresponding acids:

$$C_2H_3O.OAg + C_2H_5I = AgI + C_2H_3O.O.C_2H_5.$$

Neutral compound ethers are mostly volatile: the acid ethers are non-volatile, and as they still contain unreplaced hydrogen belonging to one or more HO groups, they act as acids, exchanging this hydrogen for metals or for alcohol-radicles.

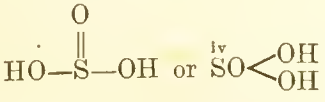
All compound ethers, but especially the acid ethers, are resolved into their components, alcohol and acid, by heating them with water, or more easily with potash or soda in aqueous or alcoholic solution:

$$\underset{\text{Ethyl acetate.}}{C_2H_3O.O.C_2H_5} + KOH = \underset{\text{Potassium acetate.}}{C_2H_3O.O.K} + \underset{\text{Ethyl alcohol.}}{C_2H_5.OH}$$

This process is called saponification, a term originally applied to the formation of soaps by boiling neutral fats (glycerin-ethers) with caustic alkali, but now extended to all similar decompositions.

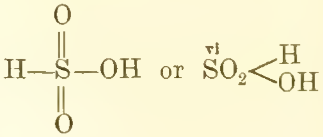
Isomerism in the Compound Ethers.—The ethers of polybasic organic acids exhibit isomeric modifications, depending on the structure of the acid itself. The most important case of this kind of isomerism is presented by the sulphurous ethers.

Sulphurous acid is susceptible of two modifications, viz.:



$$HO\!-\!\overset{\overset{\displaystyle O}{\|}}{S}\!-\!OH \text{ or } \overset{iv}{S}O{<}^{OH}_{OH}$$

Symmetrical.



$$H\!-\!\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\!-\!OH \text{ or } \overset{vi}{S}O_2{<}^{H}_{OH}$$

Unsymmetrical.

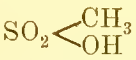
Both these modifications yield neutral alcoholic derivatives or sulphurous ethers, but only the unsymmetrical acid appears to form acid ethers, and these acid ethers are called sulphonic acids, *e.g.*:

Symmetrical:

Dimethylic sulphite, $SO{<}^{OCH_3}_{OCH_3}$

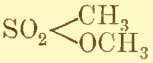
Unsymmetrical :

Methylsulphonic acid,



$SO_2<^{CH_3}_{OH}$

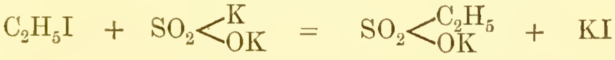
Methylic methylsulphonate,



$SO_2<^{CH_3}_{OCH_3}$

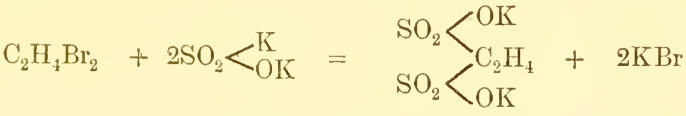
The sulphonic acids are formed by the following general reactions :

1. By heating the haloïd ethers to 120–150° with a concentrated solution of potassium or sodium sulphite ; thus :



$$C_2H_5I + SO_2<^{K}_{OK} = SO_2<^{C_2H_5}_{OK} + KI$$

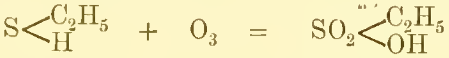
Potassium ethyl-sulphonate.



$$C_2H_4Br_2 + 2SO_2<^{K}_{OK} = \begin{matrix} SO_2\diagup OK \\ \diagdown C_2H_4 \\ SO_2\diagdown OK \end{matrix} + 2KBr$$

Potassium ethene-sulphonate.

2. By oxidation of the hydrosulphides (mercaptans) and disulphides (also of the thiocyanates) of the alcohol-radicles with nitric acid :



$$S<^{C_2H_5}_{H} + O_3 = SO_2<^{C_2H_5}_{OH}$$

$$(C_2H_5)S_2 + O_5 + H_2O = 2(C_2H_5.SO_2.OH) .$$

This mode of formation shows that the sulphur-atom of a sulphonic acid is directly united to the alcohol-radicle (and therefore to an atom of carbon), and hence it may be inferred, from the first reaction, that in the metallic sulphites an atom of metal is also directly united to the sulphur.

The sulphonic acids are very stable compounds, not decomposed by boiling with caustic alkaline solutions. When fused with potassium hydroxide, however, they are resolved into an alcohol and sulphurous acid :

$$C_2H_5.SO_2.OK + KOH = C_2H_5.OH + K.SO_2.OK .$$

By the action of phosphorus pentachlorides they are converted into acid chlorides or chloranhydrides, which, by the action of nascent hydrogen, may be converted into mercaptans :

$$C_2H_5.SO_2.OH + PCl_5 = PCl_3O + HCl + C_2H_5.SO_2.Cl$$

and $C_2H_5.SO_2.Cl + 3H_2 = HCl + 2H_2O + C_2H_5.SH .$

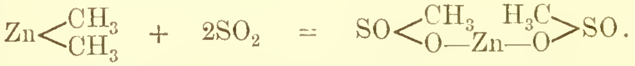
The ethers of the sulphonic acids are formed by the action of acid chlorides on the sodium-alcohols :

$$C_2H_5.SO_2.Cl + Na.OC_2H_5 = NaCl + C_2H_5.SO_2.OC_2H_5 .$$

They are identical with the neutral ethers of unsymmetrical sulphurous acid, and may accordingly be also produced by the action of silver sulphite on alcoholic iodides:

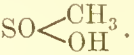
$$Ag.SO_2.OAg + 2C_2H_5I = 2AgI + C_2H_5.SO_2.O.C_2H_5 .$$

Analogous to the sulphonic acids are the sulphinic acids, or acid ethers of hyposulphurous acid, $SO<^{H}_{OH}$, the zinc salts of which are formed by the action of sulphur dioxide on the zinc-compounds of the alcohol-radicles; *e.g.*:



$$Zn<^{CH_3}_{CH_3} + 2SO_2 = SO<^{CH_3}_{O—}{}_{Zn}{}^{H_3C}_{—O}>SO .$$

By converting the zinc-salts into barium salts, and decomposing the latter with sulphuric acid, the free sulphinic acids are obtained as strongly acid liquids which decompose when heated, *e.g.*:



$$SO<^{CH_3}_{OH} .$$

The phosphorous ethers likewise exhibit isomeric modifications, derivable from symmetrical and unsymmetrical phosphorous acid, $P(OH)_3$ and $HPO(OH)_2$. The neutral ethers of symmetrical phosphorous acid are formed by the action of phosphorus trichloride on the alcohols. The ethylic ether $P(O.C_2H_5)_3$, is a liquid boiling at 191°.

Unsymmetrical phosphorous acid yields acid ethers called phosphonic acids, *e.g.*, $(C_2H_5)PO<^{OH}_{OH}$, which are formed by the action of nitric acid on the primary phosphines:

$$\underset{\text{Primary methyl phosphine.}}{CH_3.PH_2} + O_3 = \underset{\text{Methylphosphonic acid.}}{CH_3.PO(OH)_2}$$

They are crystalline bodies resembling spermaceti, dissolve in water, have a strong acid reaction, and act as bibasic acids, forming acid and neutral salts.

Hypophosphorous acid, $H_2.PO.OH$, yields analogous acid ethers, called phosphinic acids, which are formed by the action of nitric acid on the secondary phosphines; *e.g.*:

$$(CH_3)_2PH + O_2 = (CH_3)_2PO.OH .$$

Arsenious acid, AsH_3O_3, forms:

(*α.*) *Symmetrical ethers*, like $As(O.CH_3)_3$, which are produced by the action of arsenious bromide, $AsBr_3$, on the sodium alcohols; they are volatile without decomposition, and are resolved by water into arsenious acid and alcohols.

(*β.*) *Unsymmetrical ethers*, called arsonic acids, analogous to the phosphonic acids, *e.g.*, methylarsonic acid, $CH_3.AsO(OH)_2$; and lastly, there is a dimethylarsinic acid, $(CH_3)_2AsO.OH$

(cacodylic acid), analogous to the phosphinic acids (see ARSENIC BASES.

The nitrous ethers, as already observed, are isomeric with the nitroparaffins (p. 76).

The action of haloïd ethers, or of certain ethereal salts, on the hydrosulphides and sulphides of the alkali-metals, gives rise to alcoholic hydrosulphides and sulphides, that is to say, alcohols and ethers containing sulphur in place of oxygen; thus:

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + KSH = KCl + \underset{\text{Ethyl hydrosulphide.}}{C_2H_5SH}$$

$$\underset{\text{Potassium ethyl sulphate.}}{2C_2H_5OSO_3K} + \underset{\text{Potassium sulphide.}}{KSK} = \underset{\text{Potassium sulphate.}}{2KOSO_3K} + \underset{\text{Ethyl sulphide.}}{C_2H_5SC_2H_5}$$

The alcoholic hydrosulphides, or thio-alcohols, are also called mercaptans, from their property of readily combining with mercury (*corpora mercurio apta*). Their reactions are closely analogous to those of the oxygen-alcohols.

MONATOMIC ALCOHOLS AND ETHERS.

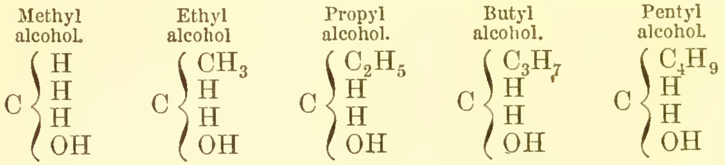
1. Containing the radicles, C_nH_{2n+1}, homologous with Methyl.

The alcohols of this series are the best known and most important of all this class of bodies. They may be formed from the corresponding haloïd ethers by the action of alkalis, and several of them are produced by the fermentation of sugar. There are also synthetical processes by which these alcohols may be built up in regular order, from the lowest upwards; but these will be better understood further on.

The names and formulæ of the known alcohols of this series are as follows:—

Methyl alcohol, ...	CH_4O
Ethyl alcohol	C_2H_6O
Propyl alcohol, ...	C_3H_8O
Butyl alcohol, ...	$C_4H_{10}O$
Pentyl or Amyl alcohol, ...	$C_5H_{12}O$
Hexyl alcohol, ...	$C_6H_{14}O$
Heptyl alcohol, ...	$C_7H_{16}O$
Octyl alcohol, ...	$C_8H_{18}O$
Nonyl alcohol, ...	$C_9H_{20}O$
Hexdecyl or Cetyl alcohol, ...	$C_{16}H_{34}O$
Ceryl alcohol, ...	$C_{27}H_{56}O$
Melissyl alcohol, ...	$C_{30}H_{62}O$

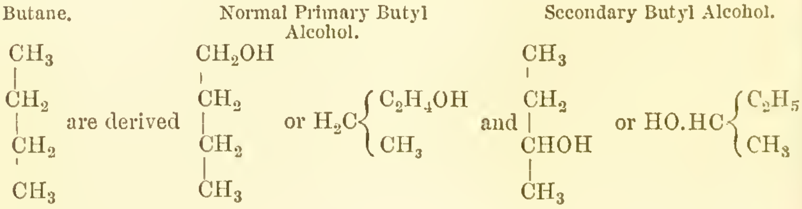
The formula of methyl alcohol is that of methane or marsh-gas having one atom of hydrogen replaced by hydroxyl; and the rest may be derived from it by replacement of one or more of the other hydrogen atoms by methyl and its homologues. If we replace only one atom of hydrogen in this manner we obtain the series:



$$\begin{array}{ccccc}\text{Methyl alcohol.} & \text{Ethyl alcohol} & \text{Propyl alcohol.} & \text{Butyl alcohol.} & \text{Pentyl alcohol.}\\ C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right. & C\left\{\begin{matrix}CH_3\\H\\H\\OH\end{matrix}\right. & C\left\{\begin{matrix}C_2H_5\\H\\H\\OH\end{matrix}\right. & C\left\{\begin{matrix}C_3H_7\\H\\H\\OH\end{matrix}\right. & C\left\{\begin{matrix}C_4H_9\\H\\H\\OH\end{matrix}\right.\end{array}$$

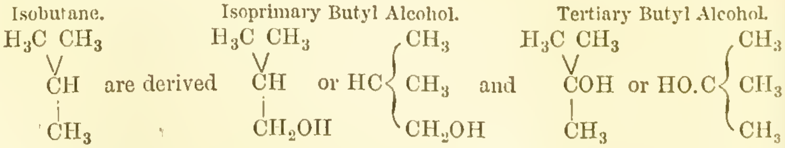
Now, it is clear that, so long as the type of an alcohol is preserved —that is, of a hydrocarbon having at least one hydrogen-atom replaced by hydroxyl—the first two alcohols of this series do not admit of any other mode of formulation: in other words, they are not susceptible of isomeric modifications. But the higher members of the series admit of isomeric modifications analogous to those of the haloïd ethers already mentioned (p. 44), and distinguished by similar names, an alcohol being designated as primary, secondary, or tertiary, according as the carbon-atom which is in combination with hydroxyl, is likewise directly united to one, two, or three other carbon-atoms. Moreover, the four-carbon-alcohol, and all above it in the series, admit of further modifications, according to the structure of the radicles (*normal* or *iso*) contained in them,—all these modifications, like those of the haloïd ethers, depending upon the structure of the paraffins from which the alcohols are derived; thus,—

From :



$$\begin{array}{ccccccc}\text{Butane.} & & \text{Normal Primary Butyl Alcohol.} & & & \text{Secondary Butyl Alcohol.} & \\ \begin{matrix}CH_3\\|\\CH_2\\|\\CH_2\\|\\CH_3\end{matrix} & \text{are derived} & \begin{matrix}CH_2OH\\|\\CH_2\\|\\CH_2\\|\\CH_3\end{matrix} & \text{or } H_2C\left\{\begin{matrix}C_2H_4OH\\CH_3\end{matrix}\right. & \text{and} & \begin{matrix}CH_3\\|\\CH_2\\|\\CHOH\\|\\CH_3\end{matrix} & \text{or } HO.HC\left\{\begin{matrix}C_2H_5\\CH_3\end{matrix}\right.\end{array}$$

and from



$$\begin{array}{ccccccc}\text{Isobutane.} & & \text{Isoprimary Butyl Alcohol.} & & & \text{Tertiary Butyl Alcohol.} & \\ \begin{matrix}H_3C\ CH_3\\ \vee\\ CH\\|\\CH_3\end{matrix} & \text{are derived} & \begin{matrix}H_3C\ CH_3\\ \vee\\ CH\\|\\CH_2OH\end{matrix} & \text{or } HC\left\{\begin{matrix}CH_3\\CH_3\\CH_2OH\end{matrix}\right. & \text{and} & \begin{matrix}H_3C\ CH_3\\ \vee\\ COH\\|\\CH_3\end{matrix} & \text{or } HO.C\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.\end{array}$$

The primary alcohols are formed by substitution of OH for H in a methyl-group CH_3; the secondary and tertiary alcohols by similar substitution in a methane group CH_2, and a methenyl-group respectively.

A very convenient nomenclature for these isomeric alcohols has been proposed by Kolbe. Methyl alcohol, $CH_3(OH)$, is called carbinol; and the alcohols formed from it by successive substitution of methyl, ethyl, &c., for an atom of hydrogen, are named according to the radicles which they contain;[*] thus,

Carbinol, or Methyl alcohol, . . .	$C(OH)H_3$
Methyl carbinol, or Ethyl alcohol, . .	$C(OH)H_2CH_3$
Ethyl carbinol, or Propyl alcohol, . .	$C(OH)H_2C_2H_5$
Dimethyl carbinol, or Pseudopropyl alcohol,	$C(OH)H(CH_3)_2$
Propyl carbinol, or Butyl alcohol, . .	$C(OH)H_2(C_3H_7)$
Isopropyl carbinol, or Isobutyl alcohol, .	$C(OH)H_2CH(CH_3)_2$
Methyl-ethyl carbinol, or Secondary Butyl alcohol, ...	$C(OH)HCH_3C_2H_5$
Trimethyl carbinol, or Tertiary Butyl alcohol,	$C(OH)(CH_3)_3$.

Primary, secondary, and tertiary alcohols are distinguished from one another by the products which they yield by oxidation. Primary alcohols of the series $C_nH_{2n+2}O$, containing the group CH_2OH, are converted by oxidation with chromic acid, first into the corresponding aldehydes $C_nH_{2n}O$ by removal of H_2, or conversion of the group CH_2OH into COH, and then by further oxidation into the corresponding acids $C_nH_{2n}O_2$ (fatty acids); thus:

$$CH_3—CH_2—CH_2OH \quad + \quad O \quad = \quad H_2O \quad + \quad CH_3—CH_2—COH$$

Normal propyl alcohol. Propyl aldehyde.

$$CH_3—CH_2—CH_2OH \quad + \quad O_2 \quad = \quad 2H_2O \quad + \quad CH_3—CH_2—COOH$$

Normal propyl alcohol. Propionic acid.

A secondary alcohol, on the other hand, which contains two alcohol-radicles united by the group CHOH, is converted, by removal of H_2 from this group, into a ketone, which is a compound consisting of two alcohol-radicles joined by the group CO; thus:

$$CH_3—CHOH—CH_3 \quad + \quad O \quad = \quad H_2O \quad + \quad CH_3—CO—CH_3$$

Secondary propyl alcohol. Dimethyl ketone.

Conversely, the aldehydes treated with nascent hydrogen (action

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[*] Odling modifies this nomenclature by restricting the term carbinol to the tertiary alcohols, designating the secondary alcohols as pseudo-alcohols or pseudols, and employing the term alcohol especially to designate the alcohols, proper or primary alcohols, which may also be called methols; thus,

	Propyl Alcohol or Ethyl-Methol.	Isobutyl Alcohol or Isopropyl-Methol.
Primary, . .	$H_2C\begin{cases} C_2H_4OH \\ CH_3 \end{cases}$	$HC\begin{cases} CH_2OH \\ CH_3 \\ CH_3 \end{cases}$
	Dimethyl Pseudol.	Ethyl-Methyl Pseudol.
Secondary, . .	$HO.CH\begin{cases} CH_3 \\ CH_3 \end{cases}$	$HO.HC\begin{cases} C_2H_5 \\ CH_3 \end{cases}$
	Trimethyl Carbinol.	Ethyl-Dimethyl Carbinol.
Tertiary, . .	$HO.C\begin{cases} CH_3 \\ CH_3 \\ CH_3 \end{cases}$	$HO.C\begin{cases} C_2H_5 \\ CH_3 \\ CH_3 \end{cases}$

of sodium amalgam) are converted into primary alcohols, and the ketones by similar treatment into secondary alcohols.

Tertiary alcohols do not yield by oxidation either aldehydes, ketones, or acids containing the same number of carbon-atoms as the alcohols themselves, but are split up into compounds containing a smaller number of carbon-atoms; tertiary butyl alcohol, for example, into formic and propionic acids:

$$(CH_3)_3.COH + O_4 = CH_2O_2 + C_3H_6O_2 + H_2O$$

METHYL ALCOHOL AND ETHERS.

Methyl Alcohol, Hydroxymethane, Carbinol, Methol, CH_4O or $CH_3(OH)$.—This is the simplest member of the series. It is produced:

1. From marsh-gas, by subjecting that compound to the action of chlorine in sunshine, whereby chloromethane, or methyl chloride, CH_3Cl, is produced, and distilling with potash.

2. From wintergreen oil, which consists chiefly of acid methyl salicylate, $C_7H_4O_3.H.CH_3$, by distillation with potash, whereby potassium salicylate is formed, and methyl alcohol distils over:

$$C_7H_4O_3.H.CH_3, + KOH = C_7H_4O_3.HK + CH_3(OH).$$

This reaction, which consists in the interchange of methyl and potassium, yields very pure methyl alcohol.

3. From crude wood-vinegar, the watery liquid obtained by the destructive distillation of wood: it was in this liquid that methyl alcohol was first discovered by P. Taylor, in 1812: hence it is often called *wood-spirit.* Crude wood-vinegar probably contains about $\frac{1}{100}$ part of methyl alcohol, which is separated from the great bulk of the liquid by distilling it, and collecting apart the first portions which pass over. The acid solution thus obtained is neutralised with slaked lime, and the clear liquid separated from the oil which floats on the surface, and from the sediment at the bottom, is again distilled. A volatile liquid is thus obtained, which burns like weak spirit; this may be strengthened by rectification, and ultimately rendered pure and anhydrous by careful distillation from quicklime at the heat of a water-bath.

Pure methyl alcohol is a thin, colourless liquid, very similar in smell and taste to ethyl alcohol; crude wood-spirit, on the other hand, which contains many impurities, has an offensive odour and a nauseous, burning taste. Methyl alcohol boils at 66·6°, and has a density of 0·798 at 20°. Vapour-density (referred to hydrogen) = 16. Methyl alcohol when pure mixes in all proportions with water: it dissolves resins and volatile oils as freely as ethyl alcohol, and is often substituted for ethyl alcohol in various processes in the arts. It may be burnt instead of ordinary spirit in lamps: the flame is pale-coloured, like that of ethyl alcohol, and deposits no soot. Methyl alcohol dissolves caustic baryta: the solution deposits, by evaporation in a vacuum, acicular crystals containing

$BaO.2CH_4O$. It dissolves calcium chloride in large quantity, and gives rise to a crystalline compound containing $CaCl_2.2CH_4O$.

Potassium and *sodium* dissolve in it, with evolution of hydrogen yielding potassium and sodium methylates, CH_3OK, and CH_3ONa.

By *oxidation*, as by exposure to the air in contact with platinum black, it is converted into formic acid, CH_2O_2, which is derived from it by substitution of 1 atom of oxygen for 2 atoms of hydrogen:

$$CH_4O + O_2 = H_2O + CH_2O_2.$$

Methyl Chloride, or Chloromethane, CH_3Cl, is formed when a mixture of equal volumes of methane (marsh-gas) and chlorine is exposed to reflected sunlight. It is more easily prepared, however, by heating a mixture of 2 parts of common salt, 1 part of wood-spirit, and 3 parts of concentrated sulphuric acid. It is a gaseous body, which may be conveniently collected over water, as it is but slightly soluble in that liquid. It is colourless; has a peculiar odour and sweetish taste, and burns, when kindled, with a pale flame, greenish towards the edges, like most combustible chlorine-compounds. Its density, referred to hydrogen as unity, is 25·25; it is not liquefied at −18°. The gas is decomposed by transmission through a red-hot tube, with slight deposition of carbon, into hydrochloric acid gas and a hydrocarbon which has been but little examined. By the action of chlorine in sunshine it is successively converted into *methene chloride*, or *dichloromethane*, CH_2Cl_2, a liquid boiling at 30·5°; *methenyl chloride*, *trichloromethane*, or *chloroform*, $CHCl_3$; and *carbon tetrachloride*, CCl_4.

Methyl Iodide, or Iodomethane, CH_3I, is a colourless and feebly combustible liquid, obtained by distilling together 1 part of phosphorus, 8 of iodine, and 12 or 15 of methyl alcohol. It is insoluble in water, has a density of 2·237, and boils at 44°. The density of its vapour, referred to hydrogen as unity, is 71. When digested in sealed tubes with *zinc*, it yields a colourless gaseous mixture containing ethane, or dimethyl, C_2H_6, and the residue contains zinc iodide, together with zinc methide, $Zn(CH_3)_2$:

$$\begin{aligned} 2CH_3I + Zn &= ZnI_2 + C_2H_6 \\ 2CH_3I + Zn_2 &= ZnI_2 + Zn(CH_3)_2 \end{aligned}$$

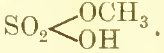
Methyl Ether, Methyl Oxide, or Methoxyl-methane, $C_2H_6O = (CH_3)_2O = C\left\{\begin{matrix} H_3 \\ OCH_3 \end{matrix}\right.$.—This compound, which bears the same relation to methyl alcohol that anhydrous potassium oxide bears to potassium hydroxide, is produced by abstraction of the elements of water from methyl alcohol: $2CH_4O - H_2O = C_2H_6O$.

It may be prepared by heating 1 part of methyl alcohol and 4 parts of concentrated sulphuric acid, and passes over as a colourless gas, which may be collected over mercury. It does not liquefy at −16°. It has an ethereal odour, and burns with a pale and feebly-luminous flame. Its specific gravity is 1·617 referred to air, or 23 referred to hydrogen as unity. Cold water dissolves about 33 times its volume of this gas, acquiring thereby its characteristic taste and odour: on boiling the solution, the gas is again liberated. Alcohol, wood-spirit, and concentrated sulphuric acid dissolve it in still larger quantity.

Methyl Nitrate, $CH_3.NO_3$, or $CH_3.O.NO_2$. This ether is obtained by distilling 50 grams of pounded nitre with 50 grams of methyl alcohol and 100 grams of sulphuric acid, in a retort without external heating. It is a colourless liquid of sp. gr. 1·182 at 20°; boils at 60°; has a faint ethereal odour. Its vapour detonates violently when heated to 150°. Heated with *alcoholic ammonia,* it yields methylamine nitrate, $CH_5N.NO_3H$. Distilled with aqueous *potash,* it yields methyl ether.

Methyl Nitrite, $CH_3.O.NO$, isomeric with nitromethane, $CH_3.NO_2$ (p. 76), is produced by the action of nitrous acid on methyl alcohol. It is a gas having a pleasant odour, and condensing at very low temperatures to a yellowish liquid which boils at $-12°$.

Methyl Sulphates.—Sulphuric acid being a bibasic acid, yields two methyl ethers—one acid, the other neutral.

Acid Methyl sulphate, Methyl and *Hydrogen sulphate, Methylsulphuric acid,* or *Sulphomethylic acid,* $CH_3.H.SO_4$, or  $SO_2{<}^{OCH_3}_{OH}$. —To prepare this acid ether, 1 part of methyl alcohol is slowly mixed with two parts of concentrated sulphuric acid, and the whole is heated to boiling, and left to cool, after which it is diluted with water, and neutralised with barium carbonate. The solution is filtered from the insoluble sulphate, and evaporated, first in a water-bath, and afterwards in a vacuum to the proper degree of concentration. The salt crystallises in beautiful, square, colourless tables, containing $(CH_3)_2Ba(SO_4)_2.2H_2O$, which effloresce in dry air, and are very soluble in water. By exactly precipitating the base from this substance with dilute sulphuric acid, and leaving the filtered liquid to evaporate in the air, methylsulphuric acid may be procured in the form of a sour, syrupy liquid, or in minute acicular crystals, very soluble in water and alcohol. It is very instable, being easily decomposed by heat. *Potassium methylsulphate.* CH_3KSO_4, crystallises in small, nacreous, deliquescent rhombic tables. The *lead salt* is also very soluble.

Neutral Methyl sulphate, or *Dimethylic sulphate,* $(CH_3)_2SO_4$, or $SO_2(OCH_3)_2$.—This ether is prepared by distilling 1 part of methyl alcohol with 8 or 10 parts of strong sulphuric acid: the distillation may be carried nearly to dryness. The oleaginous liquid found in the receiver is agitated with water, and purified by rectification from powdered anhydrous baryta. The product is a colourless, oily liquid, of alliaceous odour, having a density of 1·324, and boiling at 188°. It is neutral to test-paper, and insoluble in water, but decomposed by that liquid, slowly in the cold, rapidly and with violence at a boiling temperature, into methylsulphuric acid and methyl alcohol. Anhydrous lime and baryta have no action on this ether: their hydrates, however, and those of potassium and sodium, decompose it instantly, with production of a methylsulphate of the base, and methyl alcohol. When neutral methylsulphate is heated with common salt, it yields sodium sulphate and methyl chloride; with mercuric cyanide, or potassium cyanide, it gives a sulphate of the base and methyl cyanide; with dry sodium formate, it yields sodium sulphate and methyl formate.

Methyl Sulphite (symmetrical), $SO(O.CH_3)_2$, formed by the action of sulphur dichloride, S_2Cl_2, on methyl alcohol, is a fragrant liquid having a specific gravity of 1·045, and boiling at 121°.

Methylsulphonic Acid, $CH_3.SO_3H$, is prepared by heating methyl iodide with a concentrated solution of potassium or sodium sulphite, converting the resulting methylsulphonate into a lead-salt, decomposing the latter with hydrogen sulphide, and evaporating the filtered solution. The acid then remains as a viscid uncrystallisable liquid soluble in water. Its salts are easily soluble in water, and crystallise well; the barium salt $(CH_3.SO_3)_2.Ba$, in rhombic plates.

Methylsulphonic Chloride, $CH_3.SO_2.Cl$, boils at 153°, and is decomposed by water into hydrochloric and methylsulphonic acids.

Trichloromethylsulphonic Chloride, $CCl_3.SO_2.Cl$, is formed by the action of moist chlorine on carbon bisulphide. To prepare it, a mixture of 500 grams of hydrochloric acid, 300 grams of coarsely pounded potassium dichromate, 200 grams of nitric acid, and 30 grams of carbon bisulphide is left to itself in an open flask for about a week, water is added, and the crystals of the compound, CCl_4SO_2, are separated from the saline solution by filtration.

The chloride or chloranhydride thus formed is a colourless crystalline body, which melts at 135°, and boils at 170°. It has a camphorous tear-exciting odour, dissolves in alcohol and ether, but is insoluble in water.

Trichloromethylsulphonic Acid, $CCl_3.SO_3H$, is obtained by boiling the chloride just described with baryta-water, and decomposing the resulting barium salt with sulphuric acid. It crystallises in deliquescent prisms; the barium salt, $(CCl_3.SO_3)_2Ba + H_2O$, in laminæ.

This trichlorinated acid heated in aqueous solution with sodium-amalgam is converted successively into the acids, $CHCl_2.SO_3H$, $CH_2Cl.SO_3H$, and finally into methylsulphonic acid, $CH_3.SO_3H$. This series of reactions, discovered by Kolbe in 1845, afforded one of the earliest instances of the formation of an organic compound from inorganic materials.

Methyl Borate, $(CH_3)_3BO_3 = B(OCH_3)_3$, is formed by the action of gaseous boron chloride on anhydrous methyl alcohol. It is a limpid liquid, of specific gravity 0·9551 at 0°, boiling at 72°. Water decomposes it into boric acid and methyl alcohol.

Methyl Phosphates.—Two methyl phosphates, viz., methylphosphoric acid, $PO(OH)_2(OCH_3)$, and dimethylphosphoric acid, $PO(OH)(OCH_3)_2$, are formed by the action of phosphorus oxychloride on methyl alcohol under different circumstances.

Methyl-phosphonic Acid, $(CH_3)PO.(OH)_2$ (p. 114), is a crystalline body melting at 105°, and converted by phosphorus trichloride into methylphosphonic chloride $(CH_3)PO.Cl_2$, which melts at 32°, boils at 163°, and is reconverted into the acid by the action of water.

Dimethylphosphinic acid, $(CH_3)_2PO.OH$, is a mass resembling paraffin, melting at 76°, and volatilising without decomposition.

On *Methyl-arsonic* and *Methyl-arsinic Acids*, see ARSENIC BASES.

Methyl Silicate, $Si(OCH_3)_4$, is obtained by acting upon perfectly pure and dry methyl alcohol with silicium tetrachloride, and distilling the product. It is a colourless liquid, of pleasant, ethereal odour, specific gravity 1·0589 at 0°, distilling between 121° and 126°. It dissolves with moderate facility in water, and the solution does not become turbid, from separation of silica, for some weeks. Its observed vapour-density is 5·38 referred to air, or 77·6 referred to hydrogen, the calculated number being 76.

Methyl Hydrosulphide, CH_3SH, also called **Methyl Mercaptan.**—This compound, which has the composition of methyl alcohol with the oxygen replaced by sulphur, is formed by distilling in a water-bath, with efficient condensation, a mixture of calcium methylsulphate and potassium hydrosulphide:

$$Ca(CH_3)_2(SO_4)_2 + 2KSH = K_2SO_4 + CaSO_4 + 2CH_3SH.$$

It is a liquid lighter than water, and having an extremely offensive odour. It forms with lead-acetate a yellow precipitate, and with mercuric oxide a white compound, $(CH_3)_2S_2Hg$, which crystallises from alcohol in shining laminæ.

Methyl Sulphide, $(CH_3)_2S$, or $H_3C—S—CH_3$, is obtained by passing gaseous methyl chloride into a solution of potassium monosulphide in methyl alcohol. It is a colourless, mobile, fetid liquid, of specific gravity 0·845 at 21°, boiling at 41°. It forms several substitution-products with chlorine.

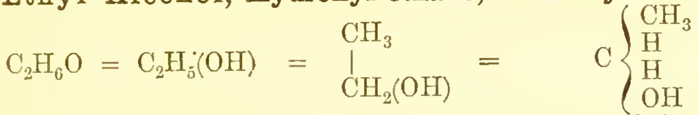
Methyl Bisulphide, $(CH_3)_2S_2$, is prepared by passing gaseous methyl chloride through an alcoholic solution of potassium bisulphide. It is a limpid, strongly refracting liquid, having a specific gravity of 1·046 at 18°, and an intolerable odour of onions; boils between 116° and 118°. It forms substitution-products with bromine and chlorine.

By substituting pentasulphide for bisulphide of potassium in the preceding preparation, a *trisulphide of methyl,* $(CH_3)_2S_3$, is obtained, boiling at about 200°.

Methyl Telluride, or **Telluro-methyl,** $(CH_3)_2Te$, obtained by distilling potassium telluride with potassium methylsulphate, is an oily fetid liquid, resembling ethyl telluride, which will be described hereafter. The corresponding selenium-compound has also been obtained.

ETHYL ALCOHOL AND ETHERS.

Ethyl Alcohol, Hydroxyl-ethane, or **Methyl Carbinol,**



$$C_2H_6O = C_2H_5(OH) = \begin{array}{c} CH_3 \\ | \\ CH_2(OH) \end{array} = C \left\{ \begin{array}{l} CH_3 \\ H \\ H \\ OH \end{array} \right.$$

This important compound, the oldest and best known of the whole group of alcohols, and generally designated by the simple name "alcohol," is produced:

1. From ethene, C_2H_4, by addition of the elements of water. When ethene gas and strong sulphuric acid are violently agitated together for a long time, the gas is absorbed, and ethylsulphuric acid, $C_2H_6SO_4$, is produced; and this compound, distilled with water, yields sulphuric acid and ethyl alcohol:

$$C_2H_6SO_4 + H_2O = H_2SO_4 + C_2H_6O.$$

Now we have seen that ethene can be formed by addition of hydrogen to acetylene, C_2H_2, which is itself formed by direct combination of carbon and hydrogen. It follows, therefore, that alcohol can be produced synthetically from its elements.

2. From ethyl chloride, bromide or iodide by the reactions already mentioned (p. 66).

3. By the fermentation of certain kinds of sugar. When a moderately warm solution of cane-sugar or grape-sugar (glucose) is mixed with certain albuminous matters, as blood, white of egg, flour-paste, and especially beer-yeast, in a state of decomposition, a peculiar process, called *fermentation*, is set up, by which the sugar is resolved into ethyl alcohol and carbon dioxide. In the case of glucose, $C_6H_{12}O_6$, these products result from a simple splitting up of the molecule:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

Cane-sugar, $C_{12}H_{22}O_{11}$, is first converted into glucose by assumption of water, ($C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$), and the latter is then decomposed as above.*

If ordinary cane-sugar be dissolved in a large quantity of water, a due proportion of active yeast added, and the whole maintained at a temperature of 21°–26° C. (70°–80° F.), the change will go on with great rapidity. The gas disengaged is nearly pure carbon dioxide: it is easily collected and examined, as the fermentation, once commenced, proceeds perfectly well in a close vessel, such as a large bottle or flask fitted with a cork and a conducting tube. When the effervescence is at an end, and the liquid has become clear, it will yield alcohol by distillation.

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* Side by side with this principal decomposition, a variety of other changes are simultaneously accomplished. According to Pasteur, glycerin, succinic acid, cellulose, fats, and occasionally lactic acid, are observed among the products of alcoholic fermentation. Some of the homologues of ethyl alcohol are also found among the products.

The spirit first obtained by distilling a fermented saccharine liquid is very weak, being diluted with a large quantity of water. By a second distillation, in which the first portions of the distilled liquid are collected apart, it may be greatly strengthened: the whole of the water cannot, however, be thus removed. The strongest rectified spirit of wine of commerce has a density of about 0·835, and yet contains 13 or 14 per cent. of water. Pure or *absolute* alcohol may be obtained from it by redistilling it with half its weight of fresh quicklime. The lime is reduced to coarse powder, and put into a retort; the alcohol is added, and the whole mixed by agitation. The neck of the retort is securely stopped with a cork, and the mixture left for several days. The alcohol is distilled off by the heat of a water-bath.

Pure alcohol is a colourless, limpid liquid, of pungent and agreeable taste and odour; its specific gravity, at 15·5° C. (60° F.), is 0·7938, and that of its vapour, referred to air, 1·613. It is very inflammable, burning with a pale-bluish flame, free from smoke; it has never been frozen. Alcohol boils at 78·4° C. (173° F.) when in the anhydrous state; in a diluted state the boiling point is higher, being progressively raised by each addition of water. In the act of dilution a contraction of volume occurs, and the temperature of the mixture rises many degrees: this takes place not only with pure alcohol, but also with rectified spirit. Alcohol is miscible with water in all proportions, and, indeed, has a great attraction for the latter, absorbing its vapour from the air, and abstracting the moisture from membranes and other similar substances immersed in it. The solvent powers of alcohol are very extensive; it dissolves a great number of saline compounds, and likewise a considerable proportion of potash. With some salts it forms definite crystalline compounds, called alcoholates: with *zinc chloride*, $ZnCl_2.2C_2H_6O$; with *calcium chloride*, $CaCl_2.4C_2H_6O$; with *magnesium nitrate*, $Mg(NO_3)_2.6C_2H_6O$. Alcohol dissolves, moreover, many organic substances, as the vegeto-alkalis, resins, essential oils, and various other bodies: hence its great use in chemical investigations and in several of the arts.

Potassium and *sodium* dissolve in ethyl alcohol in the same manner as in methyl alcohol, forming the compounds C_2H_5KO and C_3H_5NaO.

Alcohol, passed through a red-hot tube, is resolved into marsh-gas, hydrogen, and carbon monoxide:

$$C_2H_6O = CH_4 + H_2 + CO.$$

Small quantities of ethene, benzene, and naphthalene are, however, formed at the same time by the mutual action of these primary products, and carbon is deposited.

By *oxidation*, alcohol is converted, first, into aldehyde, C_2H_4O, then into acetic acid, $C_2H_4O_2$,

$$C_2H_6O + O = H_2O + C_2H_4O,$$

and

$$C_2H_4O + O = C_2H_4O_2.$$

Chlorine gas is rapidly absorbed by anhydrous alcohol, turning it yellow, and causing considerable rise of temperature. At the same time it rapidly abstracts hydrogen, which is partly replaced by the chlorine, producing hydrochloric acid, aldehyde, acetic acid, ethyl acetate, ethyl chloride, and chloral. The mixture of these substances, freed by water from the soluble constituents, was formerly called *heavy muriatic ether*. The formation of the several products is represented by the following equations:

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 = 2HCl + \underset{\text{Aldehyde.}}{C_2H_4O},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + 4Cl_2 = 5HCl + \underset{\text{Chloral.}}{C_2HCl_3O},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + HCl = H_2O + \underset{\text{Ethyl chloride.}}{C_2H_5Cl},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + H_2O + 2Cl_2 = 4HCl + \underset{\text{Acetic acid.}}{C_2H_4O_2},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Acetic acid.}}{C_2H_4O_2} = H_2O + \underset{\text{Ethyl acetate.}}{C_2H_5.C_2H_3O_2}.$$

When the action of the chlorine is continued for a long time, chloral is always the principal product. This compound is a heavy oily liquid, having the composition of aldehyde with 3 atoms of hydrogen replaced by chlorine; but it cannot be formed by the direct action of chlorine upon aldehyde. When alcohol containing water is used, scarcely any chloral is obtained, the chief product being aldehyde.

Chlorine, in presence of *alkalis*, converts alcohol into chloroform, $CHCl_3$, and carbon dioxide:

$$C_2H_6O + 5Cl_2 + H_2O = CO_2 + 7HCl + CHCl_3.$$

The same products are formed by distilling dilute alcohol with bleaching powder.

Aqueous alcohol heated with strong *sulphuric acid* is converted into ethylsulphuric acid, $C_2H_6SO_4$; but when anhydrous alcohol is exposed to the vapour of sulphuric oxide, SO_3, a white crystalline substance is formed, called ethionic oxide, formerly *sulphate of carbyl*, $C_2H_4S_2O_6$. This, when dissolved in water or in aqueous alcohol, is converted into ethionic acid, $C_2H_6S_2O_7$, a bibasic acid, which forms a soluble barium salt. Lastly, a solution of ethionic acid, when boiled, is resolved into sulphuric acid and isethionic acid, an acid isomeric with ethyl-sulphuric acid.

Commercial Spirit, Wine, Beer, &c. Vinous Fermentation.—The strength of commercial spirit, when free from sugar and other substances added subsequently to distillation, is inferred from its density: a table exhibiting the proportions of real alcohol and water in spirits of different densities will be found at the end of the volume. The excise *proof spirit* has a specific gravity of 0·9198 at 60° F., and contains 49¼ per cent. by weight of real alcohol.

The high duty on spirits of wine in this country has hitherto interfered with the development of many branches of industry, which are dependent on the free use of this important liquid. The labours of the scientific chemist have been likewise often checked by this inconvenience. A remedy for the evil has been supplied by a very important measure, proposed and carried out by the late Mr John Wood, Chairman of the Board of Inland Revenue. This measure consists in issuing, for manufacturing and scientific purposes, duty free, a mixture of 90 per cent. of spirits of wine of strength not less than corresponds with a density of 0·830, and 10 per cent. of partially purified wood-spirit, which is now sold by licensed dealers under the name of *Methylated Spirit.* It appears that a mixture of this kind is rendered permanently unfit for human consumption, the separation of the two substances, in consequence of their close analogy, being not only difficult, but to all appearance impossible: at the same time, and for the same reasons, this mixture is not materially impaired for the greater number of the more valuable purposes in the arts for which spirits are usually employed. Methylated spirit may be used, instead of pure spirit, as a solvent of resinous substances, and of many chemical preparations, especially of the alkaloïds and other organic products. It may be used for the production of fulminating mercury, ether, chloroform, iodoform, olefiant gas, and all its derivatives—in fact, for an endless number of laboratory purposes. Methylated spirit may also be substituted for pure spirit of wine in the preservation of anatomical preparations. The introduction of this spirit has already exerted a very beneficial effect upon the development of organic chemistry in this country.*

Wine, Beer, &c., owe their intoxicating properties to the alcohol they contain, the quantity of which varies very much. Port and sherry, and some other strong wines, contain from 19 to 25 per cent. of alcohol, while in the lighter wines of France and Germany it sometimes falls as low as 12 per cent. Strong ale contains about 10 per cent.; ordinary spirits, as brandy, gin, whisky, 40 to 50 per cent., or occasionally more. These latter owe their characteristic flavours to certain essential oils and compound ethers, present in very small quantity, either generated in the act of fermentation or purposely added.

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* See Report on the Supply of Spirits of Wine, free from duty, for use in the Arts and Manufactures, addressed to the Chairman of Inland Revenue by Professors Graham, Hofmann, and Redwood. (Quarterly Journal of Chemical Society, vol. viii, p. 120.)

In making wine, the expressed juice of the grape is simply set aside in large vats, where it undergoes spontaneously the necessary change. The vegetable albumin of the juice absorbs oxygen from the air, runs into decomposition, and in that state becomes a ferment to the sugar, which is gradually converted into alcohol. If the sugar be in excess, and the azotised matter deficient, the resulting wine remains sweet; but if, on the other hand, the proportion of sugar be small and that of albumin large, a *dry* wine is produced. When the fermentation stops, and the liquor becomes clear, it is drawn off from the lees, and transferred to casks, to ripen and improve.

The colour of red wine is derived from the skins of the grapes, which in such cases are left in the fermenting liquid. Effervescent wines, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure, and retained in solution in the liquid. A certain quantity of sugar is frequently added. The process requires much delicate management.

During the fermentation of the grape-juice, or *must*, a crystalline, stony matter, called *argol*, is deposited. This consists chiefly of acid potassium tartrate with a little colouring matter, and is the source of all the tartaric acid met with in commerce. The salt in question exists in the juice in considerable quantity; it is but sparingly soluble in water, but still less so in dilute alcohol: hence, as the fermentation proceeds, and the quantity of spirit increases, it is slowly deposited. The acid of the juice is thus removed as the sugar disappears. It is this circumstance which renders grape-juice alone fit for making good wine; when that of gooseberries or currants is employed as a substitute, the malic and citric acids which these fruits contain cannot be thus withdrawn. There is then no other resource but to add sugar in sufficient quantity to mask and conceal the natural acidity of the liquor. Such wines are necessarily ascescent, prone to a second fermentation, and, to many persons at least, very unwholesome.

Beer is a well-known liquor, of great antiquity, prepared from germinated grain, generally barley, and is used in countries where the vine does not flourish. The operation of *malting* is performed by steeping the barley in water until the grains become swollen and soft, then piling it in a heap or *couch*, to favour the rise of temperature caused by the absorption of oxygen from the air, and afterwards spreading it upon a floor, and turning it over from time to time to prevent unequal heating. When germination has proceeded far enough, the vitality of the seed is destroyed by kiln-drying. During this process, a peculiar nitrogenous substance called *diastase* is produced, which acts as a ferment on the starch of the grain, converting a portion of it into sugar and rendering it soluble.

In brewing, the crushed malt is infused in water at about 170° F. (77° C.), and the mixture is left to stand for two hours or more. The easily soluble diastase has thus an opportunity of acting upon the unaltered starch of the grain, and changing it into dextrin and sugar. The clear liquor, or *wort*, strained from the exhausted malt, is next pumped up into a copper boiler, and boiled with the requisite quantity of hops, to communicate a pleasant bitter flavour, and confer on the beer the property of keeping without injury. The flowers of the hop contain a bitter, resinous principle, called *lupulin*, and an essential oil.

When the wort has been sufficiently boiled, it is drawn from the copper, and cooled as rapidly as possible, to near the ordinary temperature of the air, in order to avoid an irregular acid fermentation, to which it would otherwise be liable. It is then transferred to the fermenting vessels, which in large breweries are of great capacity, and mixed with a quantity of yeast, the product of a preceding operation, by which the change is speedily induced. This is the most critical part of the whole operation, and one in which the skill and judgment of the brewer are most called into play. The process is in some measure under control by attention to the temperature of the liquid; and the extent to which the change has been carried is easily known by the diminished density, or *attenuation* of the wort. The fermentation is never suffered to run its full course, but is always stopped at a particular point, by separating the yeast, and drawing off the beer into casks. A slow and almost insensible fermentation succeeds, which in time renders the beer stronger and less sweet than when new, and charges it with carbonic acid.

Highly coloured beer is made by adding to the malt a small quantity of strongly dried or charred malt, the sugar of which has been changed to caramel; porter and stout are so prepared.

The yeast of beer is a very remarkable substance. To the naked eye it is a greenish-yellow soft solid, nearly insoluble in water, and dries up to a pale-brownish mass, which readily putrifies when moistened, and becomes offensive. Under the microscope it exhibits a kind of organised appearance, being made up of little transparent globules, which sometimes cohere in clusters or strings, like some of the lowest members of the vegetable kingdom. Whatever may be the real nature of the substance, no doubt can exist that it is formed from the soluble azotised portion of the grain during the fermentative process. No yeast is ever produced in liquids free from azotised matter; that added for the purpose of exciting fermentation in pure sugar is destroyed, and rendered inert thereby. When yeast is deprived, by straining and strong pressure, of as much water as possible, it may be kept in a cool place, with unaltered properties for a long time; otherwise it quickly spoils.

The distiller, who prepares spirits from grain, makes his wort, or *wash*, much in the same manner as the brewer; he uses, however, with the malt a large quantity of raw grain, the starch of which suffers conversion into sugar by the diastase of the malt, which is sufficent for his purpose. He does not boil his infusion with hops, but proceeds at once to the fermentation, which he pushes as far as possible by large and repeated doses of yeast. Alcohol is manufactured in many cases from potatoes. The potatoes are ground to pulp, mixed with hot water and a little malt, to furnish diastase, made to ferment, and then the fluid portion is distilled. The potato-spirit is contaminated by a very offensive volatile oil, again to be mentioned: the crude product from corn contains a substance of a similar kind. The business of the rectifier consists in removing or modifying these volatile oils, and in replacing them by others of a more agreeable character.

In making *bread*, the vinous fermentation plays an important part: the yeast added to the dough converts the small portion of sugar the meal naturally contains into alcohol and carbonic acid. The gas thus disengaged forces the tough and adhesive materials into bubbles, which are still further expanded by the heat of the oven, which at the same time dissipates the alcohol: hence the light and spongy texture of all good bread. The use of *leaven* is of great antiquity: this is merely dough in a state of incipient putrefaction. When mixed with a large quantity of fresh dough, it excites in the latter the alcoholic fermentation, in the same manner as yeast, but less perfectly; it is apt to communicate a disagreeable sour taste and odour. Sometimes carbonate of ammonia is employed to lighten the dough, being completely volatilised by the high temperature of the oven. Bread is now sometimes made by mixing a little hydrochloric acid and sodium carbonate in the dough; if proper proportions be taken and the whole thoroughly mixed, the operation appears to be very successful.

Another mode of bread-making is that invented by the late Dr. Dauglish, which consists in agitating the dough in a strong vessel with water saturated under pressure with carbonic acid gas. When the dough thus treated is subsequently released from this pressure and exposed to the air, the gas escapes in bubbles, and lightens the mass as effectually as that evolved within its substance by fermentation. The bread thus made, called "aërated bread," is of excellent quality, not being subject to the deterioration which so frequently takes place in ordinary bread, when the fermentation is allowed to go too far.

Vinous fermentation, that is to say the conversion of sugar into alcohol and carbon dioxide, never takes place except in presence of some nitrogenous body of the albuminoïd class in a state of decomposition, and it is always accompanied by the development of certain minute living organisms—fungi and infusoria—like those already mentioned as existing in yeast. So constantly indeed is this the case that many chemists and physiologists regard these organisms as the exciting cause of fermentation and putrefaction; and this view appears to be corroborated by the fact that each particular kind of fermentation takes place most readily in contact with a certain living organism, or at least with nitrogenous matter containing it; thus beer-yeast contains two species of fungus, called

Torvula cerevisiæ and *Penicillium glaucum*, the cells of which are of very different sizes, so that they may be separated by filtering an infusion of the yeast, the larger cells of the *Torvula* remaining on the filter, while those of the *Penicillium*, which are much smaller, pass through with the liquid. Now, it is found that the residue on the filter brings a solution of sugar into the state of vinous fermentation, whereas the filtered liquid induces lactous fermentation; but whether this effect is due to the fungi themselves, or to the peculiar state of the albuminous matter in which they occur, is a question not yet decided. The investigation is attended with peculiar difficulties, arising chiefly from the universal diffusion of the germs of these minute organisms, which are present not only in all decaying albuminous matter, and on the skins of fruits, leaves, and other parts of plants, but are likewise diffused through the air; so that in experiments made for the purpose of ascertaining whether fermentation can take place without them, it is extremely difficult to ensure their complete exclusion from the substances under examination.*

ETHYLIC ETHERS.

Ethyl Chloride, or **Chlorethane**, C_2H_5Cl, or $H_3C—CH_2Cl$, often called *Hydrochloric ether*.—To prepare this compound, rectified spirit of wine is saturated with dry hydrochloric acid gas, and the product distilled at a very gentle heat; or a mixture of 3 parts oil of vitriol and 2 parts of alcohol is poured upon 4 parts of dry common salt in a retort, and heat applied; in either case the vapour of the hydrochloric ether should be conducted through a little tepid water in a wash-bottle, and thence into a small receiver surrounded by ice and salt. It is purified from adhering water by contact with a few fragments of fused calcium chloride.

Ethyl chloride is a thin, colourless, and excessively volatile liquid, of a penetrating, aromatic, and somewhat alliaceous odour. At the freezing point of water, its sp. gr. is 0·921, and it boils at 12·5°. It is soluble in 10 parts of water, is but incompletely decomposed by solution of silver nitrate when the two are heated together in a sealed tube, but is quickly resolved into potassium chloride and ethyl alcohol by a hot aqueous solution of caustic potash:

$$C_2H_5Cl + KOH = KCl + C_2H_5OH.$$

With alcoholic potash, on the other hand, or potassium ethylate, it yields ethyl oxide, or common ether:

$$C_2H_5Cl + C_2H_5OK = KCl + (C_2H_5)_2O.$$

Heated with soda-lime, it yields ethene or olefiant gas:

$$2C_2H_5Cl + Na_2O = 2NaCl + H_2O + 2C_2H_4.$$

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* See the article "Fermentation," in Watts's Dictionary of Chemistry, vol. ii. p. 623.

When vapour of ethyl chloride is mixed with chlorine gas in a vessel exposed, first to diffused daylight, and afterwards to direct sunshine, hydrochloric acid is formed, and the chlorine displaces one atom of hydrogen in the ethyl chloride, producing monochlorinated ethyl chloride, ethene chloride or dichlorethane, $C_2H_2Cl_4$, (p. 70). By the prolonged action of chlorine in excess, the compounds $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6, are produced (pp. 73, 75).

Ethyl Bromide, or Bromethane, C_2H_5Br, also called *Hydrobromic ether,* is prepared by distilling a mixture of 8 parts bromine, 1 part phosphorus, and 39 parts alcohol. It is a very volatile liquid, heavier than water, having a penetrating taste and odour, boiling at 41°.

Ethyl Iodide, or Iodethane, C_2H_5I, also called *Hydriodic ether,* may be conveniently prepared with 5 parts of phosphorus, 70 parts of alcohol (of 0·84 sp. gr.), and 100 parts of iodine. The phosphorus is introduced into a tubulated retort, covered with part of the alcohol, and heated to fusion. The rest of the alcohol is poured upon the iodine, and the solution thus obtained is allowed to flow gradually through a tap-funnel into the retort. The brown liquid is at once decolorised, and ethyl iodide distils over, which is condensed by a good cooling apparatus. The distillate, consisting of alcohol and ethyl iodide, is again poured on the residuary iodine, which is thus rapidly dissolved, introduced into the retort, and ultimately entirely converted into ethyl iodide. The latter is washed with water to remove adhering alcohol, separated from this water by a tap-funnel, digested with calcium chloride, and rectified in the water-bath. Ethyl iodide may also be formed by heating in a sealed glass vessel a mixture of hydriodic acid and olefiant gas. It is a colourless liquid, of penetrating ethereal odour, having a density of 1·92, and boiling at 72°. It becomes red by exposure to light, from a commencement of decomposition. This substance has become highly important as a source of ethyl, and from its remarkable deportment with ammonia, which will be discussed in the Section on Amines.

Ethyl Oxide, or Ethylic ether, $C_4H_{10}O = C_2H_5.O.C_2H_5 = (C_2H_5)_2O$.—This compound, also called *common ether,* or simply *ether,* contains the elements of 2 molecules of alcohol *minus* 1 molecule of water:

$$2C_2H_6O - H_2O = C_4H_{10}O;$$

and it is in fact produced by the action of various dehydrating agents, such as zinc chloride, phosphoric oxide, and strong sulphuric acid, upon alcohol. The process does not appear, however, to be one of direct dehydration, at least in the case of sulphuric acid; for when that acid is heated with alcohol to a certain temperature, it does not become weaker by taking water from the alcohol, but ether and water distil over together, and the sulphuric acid remains in its original state, ready to act in the same manner on a fresh portion of alcohol. The reaction is in fact one of substitution, the ultimate result being the conversion of alcohol, $C_2H_5(OH)$, into ether, $C_2H_5(OC_2H_5)$, by the substitution of ethyl for hydrogen. The manner in which this takes place will be better understood when another mode of the formation of ether has been explained.

When a solution of sodium ethylate, $NaOC_2H_5$, in anhydrous alcohol, obtained by dissolving sodium to saturation in that liquid, is mixed with ethyl iodide, double decomposition takes place, resulting in the formation of sodium iodide and ethyl oxide:

$$NaOC_2H_5 \quad + \quad C_2H_5I \quad = \quad NaI \quad + \quad C_2H_5OC_2H_5.$$

The result would be the same if chloride or bromide of ethyl were substituted for the iodide: moreover, when methyl iodide is added, instead of the ethyl iodide, an oxygen-ether is formed containing both ethyl and methyl:

$$\underset{\text{Sodium ethylate}}{NaOC_2H_7} \quad + \quad \underset{\substack{\text{Methyl}\\\text{iodide.}}}{CH_3I} \quad = \quad NaI \quad + \quad \underset{\substack{\text{Ethyl-methyl}\\\text{ether.}}}{C_2H_5OCH_3}.$$

In each case the reaction consists in an interchange between the sodium and the alcohol-radicle.

Now, when alcohol is heated with strong sulphuric acid, the first result is the formation of ethylsulphuric acid, $SO_2(OC_2H_5)OH$, by substitution of ethyl for hydrogen in the acid:

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2(OH)(OH)} + \underset{\text{Alcohol.}}{C_2H_5(OH)} = \underset{\text{Water.}}{H(OH)} + \underset{\substack{\text{Ethylsulphuric}\\\text{acid.}}}{SO_2(OC_2H_4)(OH)};$$

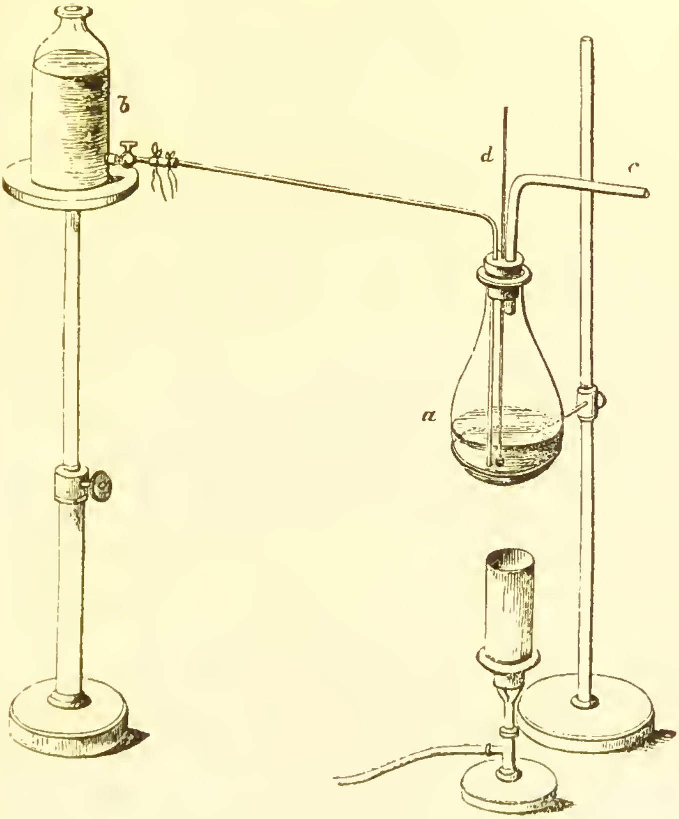
and when the ethylsulphuric acid thus formed is brought in contact, at a certain temperature, with a fresh portion of alcohol, the reverse substitution takes place, resulting in the formation of ethyl oxide and sulphuric acid:

$$\underset{\substack{\text{Ethylsulphuric}\\\text{acid.}}}{SO_2(OC_2H_5)(OH)} + \underset{\text{Alcohol}}{C_2H_5(OH)} = \underset{\text{Ether.}}{C_2H_5OC_2H_5} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2(OH)_2}.$$

The sulphuric acid is thus reproduced in its original state, and if the supply of alcohol be kept up, and the temperature maintained within certain limits, the same series of actions is continually repeated, and ether and water distil over together.

The most favourable temperature for etherification is between 127° and 154° C. (260° and 310° F.); below 127° very little ether is produced, and above 154° a different reaction takes place, resulting in the formation of olefiant gas. The maintenance of the temperature within the ether-producing limits is best effected by boiling the mixture of sulphuric acid and alcohol in a flask into which a further quantity of alcohol is supplied in a continuous and regulated stream. This is called the *continuous* ether process.

Fig. 14.



A wide-necked flask *a* (fig. 14), is fitted with a sound cork perforated by three apertures, one of which is destined to receive a thermometer with the graduation on the stem; a second, the vertical portion of a long, narrow tube, terminating in an orifice of about $\frac{1}{20}$ of an inch in diameter; and the third, a wide bent tube, *c*, connected with the condenser, to carry off the volatilised products. A mixture is made of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine, of about 0·834 sp. gr. This is introduced into the flask, and heated by a lamp. The liquid soon boils, and the thermometer very shortly indicates a temperature of 140° C. (284° F.). When this happens, alcohol of the above density is suffered slowly to enter by the narrow tube, which is put into communication with a reservoir *b*, of that liquid, consisting of a large bottle perforated by a hole near the bottom, and furnished with a small brass stopcock fitted by a cork: the stopcock is secured to the end of the long tube by a caoutchouc connector. As the tube passes nearly to the bottom of the flask, the alcohol gets thoroughly mixed with the acid liquid, the pressure of the fluid column being sufficient to ensure the regularity of the flow; the quantity is easily adjusted by the aid of the stopcock. For condensation a Liebig's condenser may be used, supplied with ice-water.

The degree of heat, and the supply of alcohol, must be so adjusted that the thermometer may remain at 140°, or as near that temperature as possible, while the contents of the flask are maintained in a state of *rapid and violent ebullition*—a point of essential importance. Ether and water distil over together, and collect in the receiver, forming two distinct strata: the mixture slowly blackens, from some slight secondary action of the acid upon the spirit, or upon the impurities in the latter, but retains, after many hours' ebullition, its etherifying powers unimpaired. The acid, however, slowly volatilises, partly in the state of *oil of wine*, and the quantity of liquid in the flask is found, after the lapse of a considerable interval, sensibly diminished. This loss of acid constitutes the only limit to the duration of the process, which might otherwise be continued indefinitely.

On the large scale, the flask may be replaced by a vessel of lead, the tubes being also of the same metal: the stem of the thermometer may be made to pass air-tight through the cover, and heat may perhaps be advantageously applied by high-pressure steam, or hot oil, circulating in a spiral tube of metal immersed in the mixture of acid and spirit.

The crude ether is to be separated from the water on which it floats, agitated with a little solution of caustic potash, and redistilled by the heat of warm water. The aqueous portion, treated with an alkaline solution, and distilled, yields alcohol containing a little ether. Sometimes the spontaneous separation before mentioned does not occur, from the accidental presence of a larger quantity than usual of undecomposed alcohol; the addition of a little water, however, always suffices to determine it.

Pure ethylic ether is a colourless, transparent, fragrant liquid, very thin and mobile. Its specific gravity at 15·5° is about 0·720; it boils at 35·6° C. (96° F.) under the pressure of the atmosphere, and bears without freezing the severest cold. When dropped on the hand it occasions a sharp sensation of cold, from its rapid volatilisation. Ether is very combustible, and burns with a white flame, generating water and carbon dioxide. Although the substance itself is one of the lightest liquids, its vapour is very heavy, having a density of 2·586 (referred to air). Mixed with oxygen gas, and fired by the electric spark, or otherwise, it explodes with the utmost violence. Preserved in an imperfectly stopped vessel, ether absorbs oxygen, and becomes acid from the production of acetic acid: this attraction for oxygen is increased by elevation of temperature. It is decomposed by transmission through a red-hot tube into ethene, methane, aldehyde, and acetylene, and two substances yet to be described.

Ether is miscible with alcohol in all proportions, but not with water; it dissolves to a small extent in that liquid, 10 parts of water taking up about 1 part of ether. It may be separated from alcohol, provided the quantity of the latter is not excessive, by addition of water, and in this manner samples of commercial ether may be conveniently examined. Ether dissolves oily and fatty substances generally, and phosphorus to a small extent, also a few saline compounds and some organic principles; but its powers in this respect are much much more limited than those of alcohol or water.

Anhydrous ether, subject to the action of chlorine, yields the three substitution-products, $C_4H_8Cl_2O$, $C_4H_6Cl_4O$, and $C_4Cl_{10}O$, the first two of which are liquids, while the third, produced by the prolonged action of chlorine on ether in sunshine, is a crystalline solid. The second chlorine compound is converted by hydrogen sulphide into the two crystalline compounds $C_4H_6Cl_2SO$ and $C_4H_6S_2O$.

Ethyl-methyl oxide, *Ethyl-methyl ether*, *Ethyl methylate*, or *Methyl ethylate*, $C_3H_8O = C_2H_5OCH_3$, is produced, as already mentioned, by the action of methyl iodide on potassium ethylate, or of ethyl iodide on potassium methylate. It is a very inflammable liquid, boiling at 11°.

Ethyl Nitrate, $C_2H_5NO_3$, or $C_2H_5ONO_2$.—*Nitric ether.*—When nitric acid is heated with alcohol alone, part of the alcohol is oxidised, and the nitric acid is reduced to nitrous acid, which, with the remainder of the alcohol, forms ethyl nitrite, $C_2H_5NO_2$, together with other products; but by adding urea to the liquid, which decomposes the nitrous acid as fast as it is formed, this action may be prevented, and the alcohol and nitric acid then form ethyl nitrate. The experiment is most safely conducted on a small scale, and the distillation must be stopped when seven-eighths of the whole have passed over; a little water added to the distilled product separates the nitric acid. Nitric ether boils at 85° or 86°, and has a density of 1·112 at 15°: it is insoluble in water, has an agreeable sweet taste and odour, and is not decomposed by an aqueous solution of caustic potash, although that substance dissolved in alcohol attacks it even in the cold, with production of potassium nitrate. Its vapour is apt to explode when strongly heated.

Ethyl Nitrite, $C_2H_5NO_2 = C_2H_5—O—NO$.—*Nitrous ether.*—This compound, isomeric with nitro-ethane, $C_2H_5—NO_2$, can be obtained pure only by the direct action of the acid itself upon alcohol. One part of starch and 10 parts of nitric acid are gently heated in a capacious retort or flask, and the vapour of nitrous acid thereby evolved is conducted into alcohol mixed with half its weight of water, contained in a two-necked bottle, which is to be plunged into cold water, and connected with a good condensing arrangement. Rise of temperature must be carefully avoided. The product of this operation is a pale-yellow volatile liquid, having an exceedingly agreeable odour of apples: it boils at 16·4°, and has a density of 0·947 at 15°. It is decomposed by potash, without darkening, into potassium nitrite and alcohol.

The *sweet spirits of nitre* of pharmacy, prepared by distilling three pounds of alcohol with four ounces of nitric acid, is a solution of nitrous ether, aldehyde, and several other substances, in spirit of wine.

Ethyl Sulphates.—There are two of these ethers, analogous to the methyl sulphates.

Acid Ethyl sulphate, Ethylsulphuric acid, or *Sulphovinic acid,* $C_2H_6SO_4 = C_2H_5.O.SO_3H = SO_2(OC_2H_5)(OH) = SO_4(C_2H_5)H$, which has the composition of sulphuric acid, SO_4H_2, with half the hydrogen replaced by ethyl, is formed by the action of sulphuric acid upon alcohol. To prepare it, strong rectified spirit of wine is mixed with twice its weight of concentrated sulphuric acid: the mixture is heated to its boiling point, and then left to cool. When cold it is diluted with a large quantity of water, and neutralised with chalk, whereby much calcium sulphate is produced. The mass is placed upon a cloth filter, drained, and pressed; and the clear solution is evaporated to a small bulk by the heat of a water-bath, filtered from a little sulphate, and left to crystallise: the product is *calcium ethylsulphate,* in beautiful, colourless, transparent crystals, containing $Ca(C_2H_5)_2(SO_4)_2.2H_2O$. They dissolve in an equal weight of cold water, and effloresce in a dry atmosphere.

Barium Ethylsulphate, $Ba(C_2H_5)_2SO_4.2H_2O$, equally soluble, and still more beautiful, may be produced by substituting, in the above process, barium carbonate for chalk. From this salt the acid may be procured by exactly precipitating the base with dilute sulphuric acid, and evaporating the filtered solution in a vacuum at the temperature of the air. It forms a sour, syrupy liquid, in which sulphuric acid cannot be recognised by the ordinary reagents, and is very easily decomposed by heat, and even by long exposure in the vacuum of the air-pump. All the ethylsulphates are soluble; the solutions are decomposed by boiling. The *lead-salt* resembles the barium-compound. The *potassium salt,* $K(C_2H_5)SO_4$—easily made by decomposing calcium ethylsulphate with potassium carbonate—is anhydrous, permanent in the air, very soluble, and crystallises well.

Potassium ethylsulphate distilled with strong sulphuric acid, yields ethyl oxide with dilute sulphuric acid, alcohol; and with strong acetic acid, ethyl acetate.

Isethionic acid, isomeric with ethylsulphuric acid, will be described amongst ethenic ethers.

Neutral Ethyl sulphate, $(C_2H_5)_2SO_4$, or $SO_2(OC_2H_5)_2$, is formed by passing the vapour of sulphuric oxide into perfectly anhydrous ether. A syrupy liquid is produced, which, when shaken with 4 volumes of water and 1 volume of ether, separates into two layers, the lower containing ethylsulphuric acid and various other compounds, while the upper layer consists of an ethereal solution of neutral ethyl sulphate. At a gentle heat the ether is volatilised, and the ethyl sulphate remains as a colourless liquid. It cannot be distilled without decomposition.

Ethyl Sulphites.—*The symmetric neutral sulphite*, $SO\!<\!\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$, is formed by the action of thionyl chloride, $SOCl_2$, or of sulphur dichloride, S_2Cl_2, on absolute alcohol:

$$SOCl_2 + 2(C_2H_5.OH) = 2HCl + SO(OC_2H_5)_2$$

$$S_2Cl_2 + 3(C_2H_5.OH) = C_2H_5.SH + 2HCl + SO(OC_2H_5)_2.$$

The mercaptan, likewise formed in the last reaction, suffers further decomposition.

Ethyl sulphite is a limpid, strong-smelling liquid, having a specific gravity of 1·085 at 0°, boiling at 161°, decomposed by water into alcohol and sulphurous acid. With *phosphorus pentachloride* it forms the chloride, $SO\!<\!\begin{smallmatrix}OC_2H_5\\Cl\end{smallmatrix}$ (isomeric with ethylsulphonic chloride), which boils at 122°, and is decomposed by water into alcohol hydrochloric acid and sulphurous acid,

When ethyl sulphite is mixed with an equivalent quantity of potassium hydroxide in dilute solution, crystalline scales are formed, consisting of the salt, $SO\!<\!\begin{smallmatrix}O.C_2H_5\\OK\end{smallmatrix}$, which may be regarded as the potassium salt of ethylsulphurous acid, isomeric with ethylsulphonic acid. The aqueous solution of this salt easily splits up into potassium sulphite and ethyl alcohol.

Ethylsulphonic acid, $C_2H_5.SO_2.OH$, formed by the action of ethyl iodide on potassium or sodium sulphite (p. 113), is a thick crystallisable liquid, which is oxidised by nitric acid to ethylsulphuric acid, $SO_4(C_2H_5)H$. Its *lead-salt*, $(C_2H_5.SO_3)_2Pb$, crystallises in easily soluble laminæ. The *ethylic ether*, $C_2H_5.SO_2.OC_2H_5$, likewise obtained by heating silver sulphite with ethyl iodide, is a liquid having a specific gravity of 1·17 at 0°, and boiling at 208°.

The *chloride*, $C_2H_5.SO_2Cl$, is a liquid boiling at 173°.

Chlorethylsulphonic acid, $C_2H_4Cl.SO_2.OH$, is produced by the action of phosphorus pentachloride on isethionic acid, $C_2H_4(OH).SO_3H$.

Ethylsulphinic acid, $C_2H_5.SO.OH$.—The zinc salt, $(C_2H_5.SO_2)_2Zn$, formed by the action of sulphur dioxide on zinc-ethide (p. 114), crystallises in shining laminæ. By oxidation with nitric acid, the acid is converted into ethylsulphonic acid.

Ethyl Phosphates.—Three ethyl orthophosphates have been obtained, two acid and one neutral, analogous in composition to the sodium phosphates; also a neutral pyrophosphate.

Monethylic Phosphate, or *Ethylphosphoric acid*, $(C_2H_5)H_2PO_4$, or $(PO)'''(OC_2H_5)(OH)_2$, also called *Phosphovinic acid.*—This acid is bibasic. Its barium salt is prepared by heating to 82° a mixture of equal weights of strong alcohol and syrupy phosphoric acid, diluting this mixture, after a lapse of 24 hours, with water, and neutralising with barium carbonate. The solution of ethylphosphate, separated by filtration from the insoluble phosphate, is evaporated at a moderate temperature. The salt crystallises in brilliant hexagonal plates, which have a pearly lustre, and are more soluble in cold than in hot water; it dissolves in 15 parts of water at 20°. The crystals contain $(C_2H_5)BaPO_4.6H_2O$. From this salt the acid may be obtained by precipitating the barium with dilute sulphuric acid, and evaporating the filtered liquid in the vacuum of the air-pump: it forms a colourless, syrupy liquid, of intensely sour taste, sometimes exhibiting appearances of crystallisation. It is very soluble in water, alcohol, and ether, and easily decomposed by heat when in a concentrated state. The ethylphosphates of calcium, silver, and lead, are but slightly soluble; those of the alkali-metals, magnesium, and strontium, are freely soluble.

Diethylic Phosphate, or *Diethylphosphoric acid*, $(C_2H_5)_2,HPO_4$, or $(PO)'''(OC_2H_5)_2(OH)$, is a monobasic acid, obtained, together with the preceding, by the action of syrupy phosphoric acid upon alcohol. Its barium, silver, and lead-salts are more soluble than the methylphosphates. The calcium salt, $(C_2H_5)_4Ca(PO_4)_2$, and the lead-salt, $(C_2H_5)_2Pb(PO_4)_2$, are anhydrous.

Triethylic Phosphate, $(C_2H_5)_3PO_4$, or $(PO)'''(OC_2H_5)_3$, is obtained in small quantity by heating the lead-salt of diethylphosphoric acid to 100°; more easily by the action of ethyl iodide on triargentic phosphate, or of phosphorus oxychloride on sodium ethylate:

$$3C_2H_5ONa + (PO)Cl_3 = 3NaCl + (PO)(OC_2H_5)_3.$$

It is a limpid liquid of specific gravity 1·072 at 12°, boiling at 215°, soluble in alcohol and ether, and also in water, by which, however, it is slowly decomposed.

Tetrethylic Pyrophosphate, $(C_2H_5)_4P_2O_7$, produced by the action of ethyl iodide on argentic pyrophosphate, is a viscid liquid of specific gravity 1·172 at 17°, decomposed by potash, with formation of potassium diethylphosphate.

Ethyl Phosphites.—*Symmetrical Triethyl Phosphite*, $P(O.C_2H_5)_3$, formed by the action of phosphorus trichloride on ethyl alcohol, boils at 191°.

Ethylphosphonic acid, $(C_2H_5)PO(OH)_2$, formed by oxidation of primary ethylphosphine with nitric acid, is a solid body melting at 44° (p.114).

Ethyl Borates.—*Triethylic Borate*, $(C_2H_5)_3BO_3$, is formed by the action of boron trichloride on alcohol:

$$3C_2H_5(OH) + BCl_3 = 3HCl + (C_2H_5)_3BO_3;$$

also, together with monethylic borate, by heating boric oxide with absolute alcohol.

It is a thin limpid liquid, of agreeable odour, specific gravity 0·885, boiling at 119°, decomposed by water. Its alcoholic solution burns with a green flame, throwing off a thick smoke of boric acid. Treated with zinc-ethyl, it yields borethyl, $B(C_2H_5)_3$, a colourless, mobile, pungent, spontaneously inflammable liquid, having a specific gravity of 0·696, and boiling at 95°.

Monethylic Borate, $C_2H_5BO_2$, is a dense inodorous liquid, having at 120° the consistence of oil of vitriol. It cannot be distilled without decomposition, being resolved at high temperatures into triethylic borate and monethylic triborate, $C_2H_5B_3O_5$, or $C_2H_5BO_2.B_2O_3$:

$$4(C_2H_5)BO_2 = (C_2H_5)_3BO_3 + (C_2H_5)B_3O_5 .$$

The latter remains as a mass resembling gum-arabic: it attracts moisture from the air, and becomes covered with a crust of boric acid.

Ethyl Silicates.—*Tetrethylic Silicate*, $(C_2H_5)_4SiO_4$, or $Si(OC_2H_5)_4$, is produced by treating silicic chloride with a small quantity of anhydrous alcohol:

$$4C_2H_5OH + SiCl_4 = 4HCl + Si(OC_2H_5)_4 .$$

It is a colourless liquid, having a rather pleasant ethereal odour, and strong peppery taste; specific gravity 0·933 at 20°. It boils without decomposition between 165° and 166°, and when set on fire burns with a dazzling flame, diffusing a white smoke of finely divided silica. It is decomposed slowly by water, quickly by ammonia and the fixed alkalis.

Silicic ethers containing ethyl and methyl, and ethyl and amyl, have likewise been obtained.

Ethylic Thio-alcohol and Ethers.

Ethyl Hydrosulphide, Ethylic Thio-alcohol, or Mercaptan, C_2H_5SH.—This compound, the sulphur analogue of ethyl alcohol, is produced, analogously to methyl hydrosulphide (p. 122), by the action of potassium hydrosulphide on calcium ethylsulphate. A solution of caustic potash of specific gravity 1·28 or 1·3, is saturated with sulphuretted hydrogen, and mixed in a retort with an equal volume of solution of calcium ethylsulphate of the same density. The retort is connected with a good condenser, and heat is applied by means of a bath of salt and water. Mercaptan and water distil over together, and are easily separated by a tap-funnel. The product thus obtained is a colourless, limpid liquid, of specific gravity 0·8325 at 21°, slightly soluble in water, easily miscible with alcohol. It boils at 36°. The vapour of mercaptan has a most intolerable odour of onions, which adheres to the clothes and person with great obstinacy: it is very inflammable, and burns with a blue flame.

When mercaptan is brought in contact with mercuric oxide, even in the cold, violent reaction ensues, water is formed, and a white substance is produced, soluble in alcohol, and separating from that liquid in distinct crystals which contain $Hg(SC_2H_5)_2$. This compound is decomposed by sulphuretted hydrogen, mercuric sulphide being thrown down, and mercaptan reproduced. By adding solutions of lead, copper, silver, and gold to an alcoholic solution of mercaptan, corresponding compounds containing those metals are formed. Caustic potash produces no effect upon mercaptan, but potassium displaces hydrogen, and gives rise to a crystallisable compound, C_2H_5SK, soluble in water. Sodium acts in a similar manner.

Ethyl Sulphides.—Three of these compounds have been obtained, analogous in composition to the methyl sulphides, and produced by similar reactions. The *monosulphide*, $(C_2H_5)_2S$, or $C_2H_5SC_2H_5$, is a colourless oily liquid, having a very pungent alliaceous odour, a specific gravity of 0·825 at 20°, and boiling at 91°. It is very inflammable, and burns with a blue flame. When poured into chlorine gas, it takes fire; but when dry chlorine is passed into a flask containing it, not at first into the liquid, the vessel being kept cool and in the shade, substitution-products are formed and hydrochloric acid is copiously evolved. The product consists chiefly of dichlorethylic sulphide, $(C_2H_4Cl)_2S$. If the action takes place in diffused daylight, and without external cooling, the compounds $(C_2H_2Cl_3)_2S$ and $(C_2HCl_4)_2S$ are obtained, which may be separated by fractional distillation, the first boiling between 189° and 192°, the second between 217° and 222°. The action of chlorine on ethyl sulphide in sunshine yields a more highly chlorinated compound, probably $(C_2Cl_5)_2S$.

Ethyl bisulphide, $(C_2H_5)_2S_2$, obtained by distilling potassium bisulphide with potassium ethylsulphate or with ethyl oxalate, is a colourless oily liquid, very inflammable, boiling at 151°. The *trisulphide*, $(C_2H_5)_2S_3$, is a heavy oily liquid, obtained by acting in like manner on potassium pentasulphide.

Triethylsulphurous Compounds.—When ethyl monosulphide and ethyl iodide are heated together, they unite and form sulphurous iodotriethide, $(C_2H_5)S.C_2H_5I$, or $S^{iv}(C_2H_5)_3I$, which crystallises in needles. The same compound is formed by the action of ethyl iodide on ethyl hydrosulphide:

$$2C_2H_5I + C_2H_5SH = HI + S(C_2H_5)_3I,$$

or of hydrogen iodide on ethyl monosulphide:

$$HI + 2(C_2H_5)_2S = C_2H_5SH + S(C_2H_5)_3I.$$

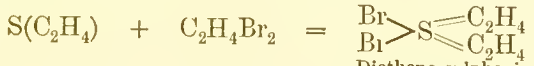
Sulphurous iodotriethide is insoluble in ether, slightly soluble in alcohol, and crystallises from the solution in white deliquescent needles belonging to the monoclinic system. It unites with metallic chlorides.

Ethyl chloride and ethyl bromide unite in like manner, but less readily, with ethyl sulphide, forming the compounds $S(C_2H_5)_3Cl$ and $S(C_2H_5)_3Br$, both of which crystallise in needles.

By treating the iodine-compound with recently precipitated silver oxide, a strongly alkaline solution is obtained, which dries up over oil of vitriol to a crystalline deliquescent mass, consisting of sulphurous triethyl-hydroxylate, $(C_2H_5)_3S(OH)$. The solution of this substance dissolves the skin like caustic potash, and forms similar precipitates with various metallic salts. It neutralises acids, forming definite crystallisable salts, *e.g.*, the *nitrate*, $(C_2H_5)_3S(ONO_2)$, the *acetate*, $(C_2H_5)_3S(OC_2H_3O)$, &c.

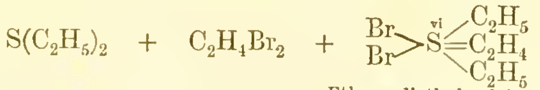
The function of the sulphur in these compounds is analogous to that of nitrogen in the ammonium-compounds. Nitrogen (quinquivalent) forms, with 4 atoms of hydrogen or of an alcohol-radicle, univalent radicles, NH_4, $N(C_2H_5)_4$, &c., which combine, like the alkali-metals, with chlorine, iodine, hydroxyl, &c.; and in like manner sulphur (quadrivalent) forms with 3 atoms of methyl, ethyl, &c., univalent radicles like $S(C_2H_5)_3$ (triethylsulphine), which also combine with chlorine, hydroxyl, &c., forming the sulphonium compounds $S^{iv}(C_2H_5)_3Cl$, $S^{iv}(C_2H_5)_3OH$, &c., the hydroxides being strong alkaline bases, like tetrethylammonium hydroxide (see p. 25; also AMINES).

Similar compounds, containing sexvalent sulphur, are obtained by combining ethyl sulphide and ethene sulphide, $S(C_2H_4)$, with ethene-dibromide; thus:



$$S(C_2H_4) + C_2H_4Br_2 = {Br \atop Br}\!>\!S\!\lessgtr\!{C_2H_4 \atop C_2H_4}$$

Diethene-sulphonium dibromide.



$$S(C_2H_5)_2 + C_2H_4Br_2 + {Br \atop Br}\!>\!\overset{vi}{S}\!\begin{matrix} C_2H_5 \\ C_2H_4 \\ C_2H_5 \end{matrix}$$

Ethene-diethyl-sulphonium dibromide.

Analogous compounds are also formed by selenium, *e.g.*, *Trimethyselenonium iodide*, $Se(CH_3)_3I$.

Ethyl Telluride, Telluric Ethide or **Tellurethyl**, $Te(C_2H_5)_2$.—This compound is obtained by distilling potassium telluride with potassium ethylsulphate:

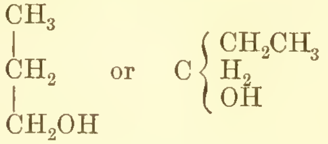
$$TeK_2 + 2K(C_2H_5)SO_4 = 2K_2SO_4 + Te(C_2H_5)_2.$$

It is a heavy, oily, yellowish-red liquid, very inflammable, and having a most intolerable odour. It acts as a bivalent radicle, uniting with chlorine, bromine, oxygen, &c., to form compounds in which the tellurium enters as a tetrad, *e.g.*, $Te(C_2H_5)_2Cl_2$, $Te(C_2H_5)_2O$, &c. The *nitrate* is obtained by treating tellurethyl with nitric acid; the other salts by double decomposition; the *chloride*, for example, settles down as a heavy oil, on adding hydrochloric acid to a solution of the nitrate. The *oxide* is best prepared by treating the chloride with water and silver oxide; it dissolves in water, forming a slightly alkaline liquid.

Selenic Ethide, or Selenethyl, $Se(C_2H_5)_2$, prepared like tellurethyl, is also a fetid liquid, exactly resembling the tellurium compound in its chemical relations.

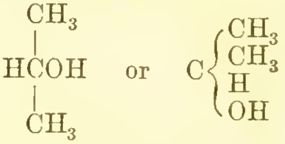
PROPYL ALCOHOLS AND ETHERS.

It has already been observed that the three-carbon alcohol, C_3H_8O, is susceptible of two isomeric modifications; namely:



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2OH \end{array} \quad \text{or} \quad C\left\{\begin{array}{l} CH_2CH_3 \\ H_2 \\ OH \end{array}\right.$$

Normal propyl alcohol.



$$\begin{array}{c} CH_3 \\ | \\ HCOH \\ | \\ CH_3 \end{array} \quad \text{or} \quad C\left\{\begin{array}{l} CH_3 \\ CH_3 \\ H \\ OH \end{array}\right.$$

Pseudopropyl alcohol.

each of which may give rise to a corresponding set of ethers.

Normal Propyl Alcohol was discovered by Chancel in 1853, in the fusel oil of the residues left in the distillation of brandy from wine. It may be obtained synthetically from ethyl alcohol by the following series of processes:—

1. Ethyl cyanide, C_3H_5N, or $CH_2CH_3.CN$ (prepared by distilling a mixture of potassium cyanide and potassium ethylsulphate, p. 92), is converted into propionic acid, $CH_2CH_3.COOH$, by boiling with strong caustic potash.

2. A mixture of the calcium salts of propionic and formic acids is subjected to dry distillation, whereby propionic aldehyde is obtained:

$$\underset{\text{Calcium propionate.}}{CH_2CH_3.COOCa'} + \underset{\text{Calcium formate.}}{H.COOCa'^{*}} = \underset{\text{Calcium carbonate.}}{Ca_2CO_3} + \underset{\text{Propionic aldehyde.}}{CH_2CH_3.COH.}$$

3. The propionic aldehyde, treated with water and sodium amalgam, takes up 2 atoms of hydrogen, and is converted into normal propyl alcohol:

$$CH_2CH_3.COH + H_2 = CH_2CH_3.CH_2OH.$$

The series of processes just described affords a general method of building up the normal primary alcohols of the fatty group, one from the other. It has not, however, been actually carried out higher than the six-carbon or hexyl alcohol.

Another method of passing from ethyl-alcohol to propyl alcohol

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* For the sake of simplicity, the equivalent (20) of calcium is used in this equation, instead of the atomic weight.

—also generally applicable as a method of synthesis of primary alcohols—is to convert ethyl cyanide or propionitril into propylamine by the action of nascent hydrogen (water and sodium amalgam) and the propylamine, by the action of nitrous acid, into propyl nitrite, which may then be converted into the alcohol by distillation with an alkali:

$$\underset{\text{Ethyl cyanide.}}{CH_3.CH_2.CN} + 2H_2 = \underset{\text{Propylamine.}}{CH_3.CH_2.CH_2.NH_2}$$

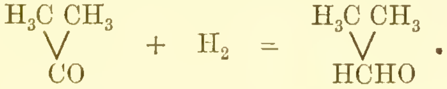
$$\underset{\text{Propylamine.}}{C_3H_7.NH_2} + 2NO_2H = 2H_2O + N_2 + \underset{\text{Propyl nitrite.}}{C_3H_7NO_2}$$

Normal propyl alcohol is an oily liquid, boiling at 96°, and having a specific gravity of 0·8205 at 0°. By oxidation with a mixture of sulphuric acid and potassium dichromate, it is converted into propionic acid.

Normal propyl chloride, C_3H_7Cl, boils at 46·5°; the *bromide* at 70°-71°; the *iodide* at 102°; the *oxide,* $(C_3H_7)_2O$, at 85°-86°.

Pseudopropyl Alcohol, or **Secondary Propyl Alcohol,** $CH(CH_3)_2OH$.—This alcohol is prepared:

1. From *acetone,* $(CO)(CH_3)_2$, by direct addition of hydrogen, evolved by the action of water on sodium amalgam:



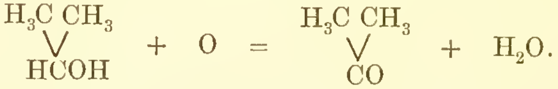
$$\underset{CO}{\overset{H_3C\ CH_3}{\vee}} + H_2 = \underset{HCHO}{\overset{H_3C\ CH_3}{\vee}}.$$

This mode of synthesis affords direct proof of the constitution of pseudopropylic alcohol, the addition of the two hydrogen-atoms being tantamount to the replacement of the bivalent radicle oxygen by the two monad radicles, hydrogen and hydroxyl.

2. Pseudopropyl iodide is prepared by the action of iodine and phosphorus on *glycerin;* this iodide is easily converted into the oxalate or acetate by treatment with silver oxalate or acetate; and from either of these ethers the alcohol may be obtained by distillation with potash or soda.

Pseudopropyl alcohol is a colourless, not very mobile liquid, having a peculiar odour, a specific gravity of 0·791 at 15°, boiling at 83° to 84° under a barometric pressure of 739 millimeters, not freezing at −20°. It does not act on polarised light. It is very difficult to dry, as it mixes with water in all proportions, and forms with it three definite and very stable hydrates, viz., $3C_3H_8O.2H_2O$, boiling at 78°-80°; $2C_3H_8O.H_2O$, boiling at 80°; and $3C_3H_8O.H_2O$, boiling at 81°. The second of these hydrates exhibits a very close resemblance to ethyl alcohol, has the same percentage composition, boils at nearly the same temperature, and likewise yields acetic acid by oxidation (see below); moreover it retains its water of hydration so obstinately, that it does not even change the white colour of anhydrous cupric sulphate to blue. The readiest mode of distinguishing between this hydrate and ethyl alcohol is to submit them to the action of iodine and phosphorus, whereby the former is converted into pseudopropyl iodide, the latter into ethyl iodide.

The characteristic property of pseudopropyl alcohol is that it yields acetone by oxidation with dilute chromic acid, this transformation being the reverse of that by which it is produced:



$$\begin{matrix} H_3C\ CH_3 \\ \vee \\ HCOH \end{matrix} + O = \begin{matrix} H_3C\ CH_3 \\ \vee \\ CO \end{matrix} + H_2O.$$

On pushing the oxidation further, the acetone breaks up into acetic acid, carbon dioxide, and water:

$$\underset{\text{Acetone.}}{CO(CH_3)_2} + O_4 = \underset{\text{Acetic acid.}}{CO(CH_3)OH} + CO_2 + H_2O.$$

The evolution of carbon dioxide in this reaction affords a further distinction between hydrated pseudopropyl alcohol and ethyl alcohol.

The formation of a ketone by oxidation is, as already observed, the essential characteristic of a secondary alcohol, and is an immediate consequence of its structure (p. 117).

Pseudopropyl alcohol, heated with acetic acid, or with potassium acetate and sulphuric acid, is converted into *pseudopropyl acetate*, $CH(CH_3)_2OC_2H_3O$.

PSEUDOPROPYL IODIDE, $CH(CH_3)_2$, is most conveniently prepared by the action of hydriodic acid, concentrated and in large excess, on glycerin (propenyl alcohol) $C_3H_8O_3$:

$$C_3H_8O_3 + 5HI = C_3H_7I + 3H_2O + 2I_2.$$

The iodine, as fast as it is set free by the reaction, may be reconverted into hydriodic acid by means of phosphorus, and will then be ready to act upon another portion of glycerin. The iodide may also be produced by the action of hydriodic acid on pseudopropyl alcohol, allyl iodide, C_3H_5I, propene, or propene alcohol.

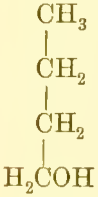
Pseudopropyl iodide is an oil boiling at 89°–90°, and having a specific gravity of 1·70. With *sodium* in presence of ether it yields propene, propane, and di-isopropyl, C_6H_{14} (p. 49). *Bromine* expels the iodine, and forms pseudopropyl bromide.

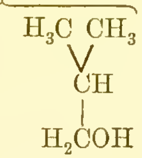
By treatment with zinc and hydrochloric acid, which evolves hydrogen, pseudopropyl iodide is converted into propane: $C_3H_7I + H_2 = HI + C_3H_8$; the propane, exposed to the action of chlorine in diffused daylight, is partly converted into normal propyl chloride; this compound, heated with potassium acetate and strong acetic acid, yields normal propyl acetate; and the latter, heated with potash-ley in sealed tubes, yields normal propyl alcohol. This series of reactions affords a general method of converting a secondary alcohol into the corresponding normal primary alcohol.

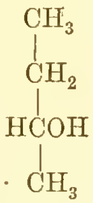
TETRYL OR BUTYL ALCOHOLS AND ETHERS.

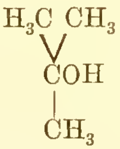
Theory indicates the existence of four alcohols included in the formula $C_4H_{10}O$, two primary, one secondary, and one tertiary; thus,

Primary. Secondary. Tertiary.


Propyl carbinol.


Isopropyl carbinol.


Methyl-ethyl carbinol.

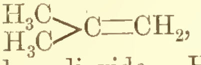
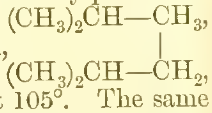

Trimethyl carbinol.

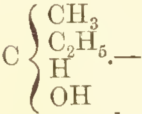
Propyl Carbinol, or Normal Butyl Alcohol, $C\left\{\begin{matrix}CH_2CH_2CH_3\\H_2\\OH\end{matrix}\right.$. —This alcohol is obtained from butyl chloride, C_4H_9Cl (produced by the action of chlorine on butane or diethyl, C_4H_{10}), by heating that chloride with potassium acetate and strong acetic acid, whereby it is converted into butyl acetate, and treating that compound with barium hydrate. It may also be prepared from normal propyl alcohol, in the same manner as the latter is obtained from ethyl alcohol, viz., by successive conversion into propyl cyanide or butyronitril, C_4H_7N or $CH_2CH_2CH_3.CN$, normal butyric acid, $CH_2CH_2CH_3.COOH$, butyric aldehyde, $CH_2CH_2CH_3.COH$ (prepared by heating a mixture of the calcium salts of butyric and formic acids), and finally into the alcohol, $CH_2CH_2CH_3.CH_2OH$, by the action of nascent hydrogen on the aldehyde; or, lastly, by converting the butyronitril into butylamine, $C_4H_{11}N$, the latter into butyl nitrite by the action of nitrous acid, and distilling the nitrite with an alkali.

Normal butyl alcohol boils at 115°, smells like isobutyl alcohol, is much lighter than water, slightly soluble therein; with iodine and phosphorus it yields normal butyl iodide, boiling at 127°. Oxidation with dilute chromic acid converts it into normal butyric acid $CH_2CH_2CH_3.COOH$.

Isopropyl Carbinol, or Isobutyl Alcohol, $C\left\{\begin{matrix}CH(CH_3)_2\\H_2\\OH\end{matrix}\right.$ —This variety of primary butyl-alcohol was found by Wurtz in the fusel-oil obtained by fermenting the molasses of beet-root sugar. To separate it, this oil is submitted to fractional distillation, and the liquid boiling between 108° and 118° is repeatedly rectified over potassium hydroxide, till it boils constantly at 110°.

Pure isobutyl alcohol is a colourless liquid, having an odour somewhat like that of amyl alcohol, but less pungent, and more vinous: specific gravity = 0·8032 at 18·5°. It dissolves in 10½ times its weight of water, and is separated therefrom, as an oil, by calcium chloride, sodium chloride, and other soluble salts. By oxidation it is converted into isobutyric acid, $CH(CH_3)_2.COOH$.

Isobutyl alcohol is acted upon by acids and other chemical reagents much in the same manner as common alcohol. With strong *sulphuric acid* it yields isobutyl-sulphuric acid, $(C_4H_9)HSO_4$, if the mixture is kept cool; but on heating the liquid, isobutene,  $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C{=}CH_2$, is given off mixed with sulphurous oxide and carbon dioxide. Heated with *hydrochloric acid* in a sealed tube, or treated with *phosphorus pentachloride* or *oxychloride*, it is converted into isobutyl chloride or chloro-isobutane, $(CH_3)_2CH{-}CH_2Cl$, an ethereal liquid, having a pungent odour, and boiling at 70°. Isobutyl bromide, C_4H_9Br, obtained in like manner, boils at 89°, the iodide, C_4H_9I, at 121°. The iodide is decomposed by potassium or sodium, yielding iso-octane or iso-dibutyl,  $\begin{matrix}(CH_3)_2CH{-}CH_3,\\ \quad\quad\quad\quad|\\ (CH_3)_2CH{-}CH_2,\end{matrix}$ a limpid liquid, lighter than water, and boiling at 105°. The same hydrocarbon is obtained by the electrolysis of ordinary valeric acid, $C_5H_{10}O_2$.

Methyl-ethyl Carbinol, or Secondary Butyl Alcohol,  $C\left\{\begin{matrix}CH_3\\C_2H_5\\H\\OH\end{matrix}\right.$.—This alcohol is obtained from erythrite, a saccharine substance having the composition of a tetratomic alcohol, $C_4H_{10}O_4$, or $C_4H_6(OH)_4$. The erythrite, distilled with fuming hydriodic acid, yields methyl-ethyl-iodomethane, or secondary butyl iodide, $C(CH_3)(C_2H_5)HI$, and this liquid, treated with moist silver oxide is converted into methyl-ethyl carbinol:

$$C(CH_3)(C_2H_5)HI + AgOH = AgI + C(CH_3)(C_2H_5)HOH.$$

Methyl-ethyl-carbinol is a colourless oily liquid, having a strong odour and burning taste, a specific gravity of 0·85 at 0°, and boiling at 95°–98° (about 20° lower than the normal primary alcohol). When heated at 250°, it is for the most part resolved into water and butene: $C_4H_{10}O = H_2O + C_4H_8$.

Methyl-ethyl-iodomethane, or *Secondary Butyl iodide*, prepared as above, or by the action of strong hydriodic acid on the alcohol, is a liquid having a pleasant ethereal odour, a specific gravity of 1·632 at 0°, 1·600 at 20°, and 1·584 at 30°. It boils at 118°. Bromine decomposes it, expelling the iodine and forming butene dibromide,

$C_4H_8Br_2$. When distilled with alcoholic potash, it gives off butene. This tendency to give off the corresponding olefine is characteristic of all the secondary alcohols and ethers, as will be further noticed in connection with the five-carbon compounds.

Trimethyl Carbinol, or Tertiary Butyl Alcohol, $C\left\{\begin{matrix}(CH_3)_3\\OH\end{matrix}\right.$, is produced by treating zinc methide with carbonyl chloride (phosgene gas) or acetyl chloride, and submitting the product to the action of water.

$$\begin{array}{ccccccc}
2COCl_2 & + & Zn(CH_3)_2 & = & ZnCl_2 & + & 2COCH_3Cl \\
\text{Carbonyl chloride.} & & \text{Zinc methide.} & & \text{Zinc chloride.} & & \text{Acetyl chloride.} \\
COCH_3Cl & + & Zn(CH_3)_2 & = & ZnO & + & C\left\{\begin{matrix}(CH_3)_3\\Cl\end{matrix}\right. \\
\text{Acetyl chloride.} & & \text{Zinc methide.} & & \text{Zinc oxide.} & & \text{Trimethyl chloromethane.} \\
C\left\{\begin{matrix}(CH_3)_3\\Cl\end{matrix}\right. & + & HOH & = & HCl & + & C\left\{\begin{matrix}(CH_3)_3\\OH\end{matrix}\right. \\
\text{Trimethyl chloromethane.} & & \text{Water.} & & & & \text{Trimethyl carbinol.}
\end{array}$$

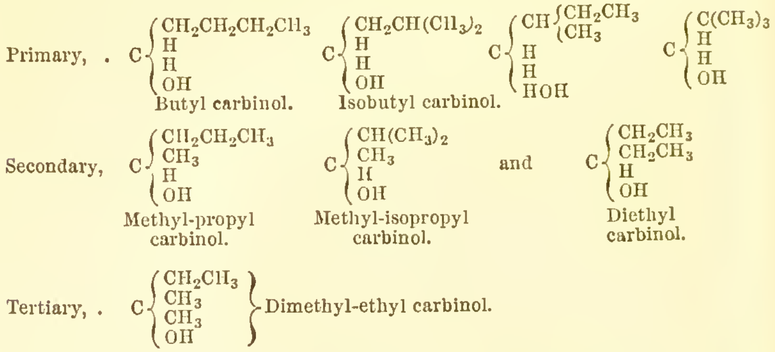
It may also be formed from the primary isoalcohol by the following series of processes:—(1.) The alcohol treated with sulphuric acid, or other dehydrating agent, yields isobutene, C_4H_8.—(2.) This olefine, treated with strong hydriodic acid, yields tertiary butyl iodide, the iodine attaching itself to the carbon-atom which is not in direct combination with hydrogen.—(3.) The iodide treated with silver oxide is converted into the tertiary alcohol. The series of transformations is represented by the following formulæ:—

$$\begin{array}{cc}
(CH_3)_2CH—CH_2OH & (CH_3)_2C=CH_2 \\
\text{Isobutyl alcohol.} & \text{Isobutene.} \\
(CH_3)_2CI—CH_3 & (CH_3)_2C(OH)—CH_3 \\
\text{Tertiary Butyl iodide.} & \text{Tertiary Butyl alcohol.}
\end{array}$$

Trimethyl carbinol, when perfectly anhydrous, crystallises in rhombic prisms or tables, melting at 25·5°. In the liquid state it has a specific gravity of 0·7788 at 30°, and boils at 82·5°. It mixes with water in all proportions, and likewise forms a definite hydrate, $2C_4H_{10}O.H_2O$, which crystallises in a freezing mixture, and boils without decomposition at 80°. By oxidation with chromic acid, trimethyl carbinol is resolved into acetic acid and acetone, together with a small quantity of isobutyric acid.

PENTYL ALCOHOLS AND ETHERS.

The formula $C_5H_{12}O$ may include eight different alcohols: four, primary, three secondary, and one tertiary, viz.:—



Primary, .	$C\begin{cases}CH_2CH_2CH_2CH_3\\H\\H\\OH\end{cases}$ Butyl carbinol.	$C\begin{cases}CH_2CH(CH_3)_2\\H\\H\\OH\end{cases}$ Isobutyl carbinol.	$C\begin{cases}CH\begin{cases}CH_2CH_3\\CH_3\end{cases}\\H\\H\\HOH\end{cases}$	$C\begin{cases}C(CH_3)_3\\H\\H\\OH\end{cases}$
Secondary,	$C\begin{cases}CH_2CH_2CH_3\\CH_3\\H\\OH\end{cases}$ Methyl-propyl carbinol.	$C\begin{cases}CH(CH_3)_2\\CH_3\\H\\OH\end{cases}$ Methyl-isopropyl carbinol.	and	$C\begin{cases}CH_2CH_3\\CH_2CH_3\\H\\OH\end{cases}$ Diethyl carbinol.
Tertiary, .	$C\begin{cases}CH_2CH_3\\CH_3\\CH_3\\OH\end{cases}$ Dimethyl-ethyl carbinol.			

Six of these are known, viz., the first, second, fifth, sixth, seventh and eighth.

Butyl Carbinol or **Normal Primary Pentyl Alcohol**, $H_2C\begin{cases}C_3H_6OH\\CH_3\end{cases}$, is prepared from normal butyl alcohol in the same manner as the latter from normal propyl alcohol, viz., by successive conversion into butyl cyanide $CH_2CH_2CH_2CH_3.CN$, normal valeric acid $CH_2CH_2CH_2CH_3.COOH$, valeric aldehyde $CH_2CH_2CH_2CH_3.COH$, and the alcohol $CH_2CH_2CH_2CH_3.CH_2OH$. It is a liquid boiling at 135°, *i.e.*, 3 degrees higher than isopentyl alcohol. The chloride, bromide, iodide, and acetate obtained from it boil at higher temperatures than the corresponding isopentyl compounds. By oxidation it yields normal valeric acid.

Isobutyl Carbinol, Isopentyl Alcohol, or **Amyl Alcohol**, $CH\begin{cases}(C_2H_4OH\\(CH_3)_2\end{cases}$.—This is the ordinary amyl alcohol produced by fermentation. In the manufacture of brandy from corn, potatoes, or the must of grapes, the ethyl alcohol is found to be accompanied by an acrid oily liquid called *fusel-oil*, which is very difficult to separate completely from the ethyl alcohol. It passes over, however, in considerable quantity towards the end of the distillation, and may be collected apart, washed by agitation with several successive portions of water to free it from ethyl alcohol, and re-distilled. The liquid thus obtained consists chiefly of amyl alcohol, sometimes mixed with propylic, butylic, and other alcohols. The amyl alcohol may be obtained pure by fractional distillation, the portion which passes over between 128° and 132° being collected apart. Potato fusel-oil consists almost wholly of ethyl and amyl alcohols, the latter constituting the greater quantity.

Amyl alcohol is an oily, colourless, mobile liquid, having a peculiar odour, and a burning acrid taste. Its vapour when inhaled produces coughing and oppression of the chest. It has a specific gravity of 0·825 at 0°, and boils at 130°. When dropped on paper it forms a greasy stain, which, however, disappears after a while. It is not perceptibly soluble in water, but floats on the surface of that liquid like an oil; common alcohol, ether, and various essential oils dissolve it readily.

Amyl alcohol usually exerts a rotatory action on polarised light, but the rotatory power varies considerably in different samples. Pasteur, indeed, has shown that ordinary amyl alcohol is a mixture of two isomeric alcohols, having the same vapour-density, but differing in their optical properties, one of them turning the plane of polarisation to the right, whereas the other is optically inactive, They are separated by converting the crude amyl alcohol into amylsulphuric acid, saturating with barium carbonate, and crystallising the barium amylsulphate thus formed. The salt obtained from the active amyl alcohol is 2½ times more soluble than that obtained from the inactive alcohol, and consequently the latter crystallises out out first; and by precipitating the barium from the solution of either salt with sulphuric acid, and distilling the amylsulphuric acid thus separated with water, the corresponding amyl alcohol is obtained. The difference of optical character between the two alcohols—which is traceable through many of their derivatives—has not been satisfactorily explained; but it perhaps depends upon the arrangement of the molecules, rather than upon that of the atoms within the molecule. On the other hand, it is possible that the active and inactive alcohols may contain different radicles, as indicated by the second, third, and fourth formulæ of primary amyl alcohols above given.

Vapour of amyl alcohol passed through a red-hot tube, yields a mixture of ethene, propene, butene, and isopentene or amylene.

Amyl alcohol takes fire easily and burns with a blue flame. When exposed to the air in contact with platinum black, or treated with a mixture of potassium chromate and dilute sulphuric acid, it is oxidised to isovaleric acid, $CH_2CH(CH_3)_2.COOH$.

Amyl alcohol, heated to 220° with a mixture of *potassium hydroxide* and *lime*, is converted into potassium valerate, with evolution of hydrogen:

$$C_5H_{12}O \quad + \quad KHO \quad = \quad C_5H_9KO_2 \quad + \quad 2H_2.$$

Potassium and *sodium* dissolve in amyl alcohol as in ethyl alcohol, yielding the compounds, $C_5H_{11}KO$, and $C_5H_{11}NaO$, which, when treated with amyl iodide, yield amyl oxide or amyl ether, $(C_5H_{11})_2O$, and with ethyl iodide, ethyl-amyl oxide, $(C_2H_5)(C_5H_{11})O$.

Chlorine acts upon amyl alcohol as upon ethyl alcohol (p. 125), excepting that it finally removes only four atoms of hydrogen, instead of five:

$$\underset{\text{Amyl alcohol.}}{C_5H_{12}O} \quad + \quad 3Cl_2 \quad = \quad 4HCl \quad + \quad \underset{\text{Chloramylal.}}{C_5H_8Cl_2O}$$

Amyl alcohol is acted upon by acids, like common alcohol, yielding ethers. When mixed with strong *sulphuric acid*, it is converted into amyl-sulphuric acid, $(C_5H_{11})HSO_4$; and, on distilling the mixture, amyl oxide, $(C_5H_{11})_2O$, passes over, together with amylene, and several other hydrocarbons.

ISOPENTYL CHLORIDE, or AMYL CHLORIDE, $C_5H_{11}Cl$, or $HC\left\{\begin{matrix} C_2H_4Cl \\ (CH_3)_2 \end{matrix}\right.$, is prepared by distilling equal weights of amyl alcohol and phosphorus pentachloride, washing the product repeatedly with alkaline water, and rectifying it from calcium chloride. Less pure it may be obtained by saturating amyl alcohol with hydrochloric acid. It is a colourless liquid, of agreeable aromatic odour, insoluble in water, and neutral to test-paper: it boils at 102°, and ignites readily, burning with a flame green at the edges. By the long continued action of chlorine, aided by powerful sunshine, it is converted into octochlorinated amyl chloride, or nonochloropentane, $C_5H_3Cl_9$, a volatile, colourless liquid, smelling like camphor: the whole of the hydrogen has not yet, however, been removed. The *bromide*, $C_5H_{11}Br$, is a volatile, colourless liquid, heavier than water, boiling at 119°. It is obtained by distilling amyl alcohol with bromine and phosphorus (see Ethyl bromide, p. 131). Its odour is penetrating and alliaceous. The bromide is decomposed by an alcoholic solution of potash, with reproduction of the alcohol and formation of potassium bromide. The *iodide*, $C_5H_{11}I$, is prepared by distilling a mixture of 15 parts of amyl alcohol, 8 of iodine, and 1 of phosphorus. It is colourless when pure, heavier than water, volatile without decomposition at 146°, and in other respects resembles the bromide: it is partly decomposed by exposure to light. Heated to 290° in sealed tubes, with zinc, it yields decane or diamyl, $C_{10}H_{22}$, or $C_5H_{11}.C_5H_{11}$, a colourless ethereal liquid boiling at 155°. At the same time there is formed a compound of zinc iodide with zinc amylide, $Zn(C_5H_{11})_2$, which is decomposed by contact with water, yielding zinc oxide and pentane or amyl hydride (p. 48):

$$Zn(C_5H_{11})_2 + H_2O = ZnO + 2C_5H_{12}.$$

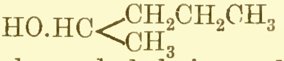
AMYL OXIDE, $(C_5H_{11})_2O$, obtained by the processes already mentioned, is a colourless oily liquid, of specific gravity 0·779, and boiling at 176°.

AMYLSULPHURIC, or SULPHAMYLIC ACID, $(C_5H_{11})HSO_4$, or $C_5H_{11}(OSO_3H)$. The barium salt of this acid, $(C_5H_{11})_2Ba(SO_4)_2$ 2 aq., prepared like the ethylsulphate (p. 136), crystallises, on evaporating the solution, in small brilliant pearly plates; the difference of solubility of the salts prepared from optically active and optically inactive amyl alcohol has already been mentioned. The barium may be precipitated from the salt by dilute sulphuric acid, and the sulphamylic acid concentrated by spontaneous evaporation to a syrupy, or even crystalline state: it has an acid and bitter taste, strongly reddens litmus-paper, and is decomposed by ebullition into amyl alcohol and sulphuric acid. The potassium salt forms groups of small radiated needles, very soluble in water. The sulphamylates of calcium and lead are also soluble and crystallisable.

Amyl hydrosulphide, $C_5H_{11}SH$, and Amyl sulphide, $(C_5H_{11})_2S$, resemble the ethyl-compounds in their properties and reactions.

Fusel-oil of Grain-spirit.—The fusel-oil, separated in large quantities from grain-spirit by the London rectifiers, consists chiefly of amyl alcohol mixed with ethyl alcohol and water. Sometimes it contains in addition more or less of the ethyl- or amyl-compounds of certain fatty acids thought to be identical with œnanthylic and palmitic acids. These last-named substances form the principal part of the nearly solid fat produced in this manner in whisky distilleries conducted on the old plan. Mulder has described, under the name of *corn-oil*, another constituent of the crude fusel-oil of Holland; it has a very powerful odour, resembling that of some of the umbelliferous plants, and is unaffected by solution of caustic potash. According to Mr. Rowney, the fusel-oil of the Scotch distilleries contains in addition a certain quantity of capric acid, $C_{10}H_{20}O_2$. Amyl alcohol, in addition to isobutyl alcohol, has been separated from the spirit distilled from beet-molasses and from artificial grape-sugar made by the aid of sulphuric acid.

Propyl-methyl Carbinol,

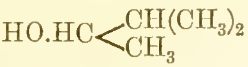


$HO.HC{<}\genfrac{}{}{0pt}{}{CH_2CH_2CH_3}{CH_3}$, or, $C_3H_7—CHOH—CH_3$.—This secondary alcohol is produced by decomposing propyl-methyl ketone (obtained by distilling a mixture of calcium butyrate and acetate) with water and sodium amalgam:

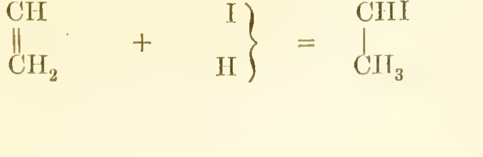
$$C_3H_7—CO—CH_3 + H_2 = C_3H_7—CHOH—CH_3 .$$

It is a liquid smelling like ordinary amyl alcohol, but less pungent; boils at 120°; has a specific gravity of 0·825 at 0°; is oxidised by potassium permanganate to propyl-methyl ketone.

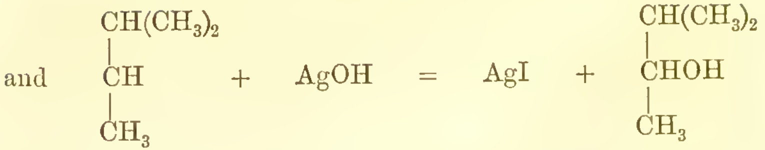
Isopropyl-methyl Carbinol,



$HO.HC{<}\genfrac{}{}{0pt}{}{CH(CH_3)_2}{CH_3}$, also called **Amylene hydrate,** $(C_5H_{10})\left\{\begin{matrix}H\\OH\end{matrix}\right.$.—This is a secondary alcohol produced from amylene, C_5H_{10}, by combining that substance with hydriodic acid, and decomposing the resulting hydriodide, $C_5H_{10}.HI$, with moist silver oxide, whereby silver iodide and amylene hydrate are obtained:



$$\begin{matrix}CH(CH_3)_2\\ |\\ CH\\ \|\\ CH_2\end{matrix} \quad + \quad \left.\begin{matrix}I\\H\end{matrix}\right\} = \begin{matrix}CH(CH_3)_2\\ |\\ CHI\\ |\\ CH_3\end{matrix}$$



$$\text{and}\quad \begin{array}{l}CH(CH_3)_2\\ |\\ CH\\ |\\ CH_3\end{array} \quad + \quad AgOH \quad = \quad AgI \quad + \quad \begin{array}{l}CH(CH_3)_2\\ |\\ CHOH\\ |\\ CH_3\end{array}$$

A portion of the hydriodide is at the same time resolved, by the heat evolved in the reaction, into hydriodic acid and amylene; and, on submitting the resulting liquid to fractional distillation the amylene passes over first, and then, between 105° and 108°, the amylene hydrate or isopropyl-methyl carbinol.

This alcohol is a liquid having a specific gravity of 0·829 at 0°, and a pungent ethereal odour, quite distinct from that of ordinary amyl alcohol. Heated with strong *sulphuric acid*, it is converted, not into amylsulphuric acid, but into hydrocarbons polymeric with amylene, viz., diamylene, or decene, $C_{10}H_{20}$, and triamylene, or pentadecene, $C_{15}H_{30}$ (p. 55). *Hydriodic acid* converts it, at ordinary temperatures, into amylene hydriodide, $C_5H_{10}.HI$, boiling at 130° (amyl iodide at 146°). *Hydrochloric acid* converts it (even at 0°) into amylene hydrochloride, $C_5H_{10}.HCl$, having a boiling point 10° below that of amyl chloride. On mixing it with two atoms of *bromine* at a very low temperature, a red liquid is formed, which, as soon as it attains the ordinary temperature of the air, is resolved into water and amylene bromide. Heated for some time to 100° with strong *acetic acid*, it yields amylene, together with a small quantity of amylene acetate. *Sodium* dissolves in amylene hydrate with evolution of hydrogen, forming a colourless translucent mass, which has the composition $C_5H_{10}NaOH$, and is decomposed by amylene hydriodide in the manner shown by the equation:

$$\underset{\text{Sodium compound.}}{C_5H_{10}NaOH} + \underset{\text{Amylene hydriodide.}}{C_5H_{10}HI} = \underset{\text{Amylene.}}{C_5H_{10}} + \underset{\text{Amylene hydrate.}}{C_5H_{10}H(OH)} + NaI$$

From these reactions it is apparent that amylene hydrate or isopropyl-methyl carbinol is especially distinguished from the primary amyl alcohols by the facility with which it gives up the corresponding olefine. This peculiarity is exhibited also by all the secondary alcohols of the series. These alcohols may indeed be regarded as intermediate links between the primary monatomic alcohols and the diatomic alcohols or glycols, *e.g.*,

$$\underset{\text{Amyl alcohol.}}{C_5H_{11}(OH)} \qquad \underset{\text{Amylene hydrate.}}{C_5H_{10}\left\{\begin{array}{l}H\\ OH\end{array}\right.} \qquad \underset{\text{Amylene glycol.}}{C_5H_{10}\left\{\begin{array}{l}OH\\ OH\end{array}\right.}$$

Diethyl Carbinol, $C_2H_5—CHOH—C_2H_5$, is produced by heating ethyl formate with ethyl iodide and granulated zinc, and decomposing the product with ice-cold water. The action of the zinc on the ethyl iodide produces zinc-ethyl, and this reacts with the ethyl formate according to the following equation:

$$HCO.OC_2H_5 + 2Zn(C_2H_5)_2 = HC\left\{\begin{array}{l}(C_2H_5)_2\\ ZnOC_2H_5\end{array}\right. + Zn\left\{\begin{array}{l}C_2H_5\\ OC_2H_5\end{array}\right. ;$$

and on treating this product with water, the compound, $HC\left\{\begin{array}{l}(C_2H_5)_2\\ ZnOC_2H_5\end{array}\right.$ is decomposed, yielding diethyl carbinol, together with zinc-hydroxide and ethene,

$$HC\left\{\begin{array}{l}(C_2H_5)_2\\ ZnOC_2H_5\end{array}\right. + 2H_2O = HOCH\left\{\begin{array}{l}C_2H_5\\ C_2H_5\end{array}\right. + Zn(OH)_2 + C_2H_6$$

The final result is the replacement of the oxygen-atom of the group HO, in formic acid, HCO.OH, by 2 atoms of ethyl.

Diethyl carbinol is a liquid which smells like amyl alcohol, has a specific gravity of 0·832 at 0°, and boils at 116–117°. By oxidation with chromic acid, it is converted with diethyl ketone, $CO(C_2H_5)_2$. The corresponding iodide boils at 145°; the acetate at 132°.*

Ethyl-dimethyl Carbinol, or Tertiary Amyl Alcohol, $C\left\{\begin{array}{l}C_2H_5\\ (CH_3)_2\\ OH\end{array}\right.$, is prepared like tertiary butyl alcohol, by treating zinc-methide with propionyl chloride, C_3H_5OCl, and decomposing the product with water. It smells very much like tertiary butyl alcohol, has a specific gravity of 0·828 at 0°, solidifies to a crystalline mass at −30°, boils between 98·5° and 100°, and does not solidify at −17°, but merely becomes viscid. By oxidation with dilute chromic acid, it yields nothing but acetic acid.

The boiling points of the six known pentyl alcohols become gradually lower, from the normal primary to the tertiary, as their structure becomes more complex; thus:

		Boiling point.
Primary,	Butyl carbinol, ...	137°
	Isobutyl carbinol, ...	128°–132°
Secondary,	Propyl-methyl carbinol, . .	120°–123°
	Diethyl carbinol, ...	116°–117°
	Isopropyl-methyl carbinol, . .	104°–108°
Tertiary,	Ethyl-dimethyl carbinol, . .	98·5°–100°

HEXYL ALCOHOLS AND ETHERS.

The number of possible modifications of an alcohol increases with the number of carbon-atoms in its molecular formula. Thus we have seen that there may be two propyl alcohols, C_3H_8O, four butyl alcohols, $C_4H_{10}O$, and eight amyl alcohols, $C_5H_{12}O$. The six-carbon formula, $C_6H_{14}O$, will in like manner be found to include seventeen isomeric alcohols—eight primary, six secondary, and three tertiary; but as the manner in which these modifications arise has been sufficiently explained in the preceding pages, the further development of the theoretical formulæ may be left as an exercise for the student.

The number of modifications of the six-carbon alcohol actually known is eight: of which two are primary, three secondary, and the remaining three tertiary.

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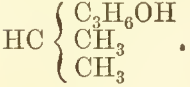
* Wagner, Liebig's Annalen, clxxv. 351; Chem. Soc. J. 1875, p. 627.

Primary Hexyl Alcohols, $C_6H_{13}(OH)$.—The normal alcohol, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2OH$, or $H_2C\left\{\begin{array}{l}C_4H_8OH\\CH_3\end{array}\right.$, is obtained, from the essential oil of *Heracleum giganteum*, which is a mixture of hexyl butyrate and octyl acetate. The hexyl and octyl alcohols are isolated by decomposing the oil with alcoholic potash, and separated by fractional distillation. The hexyl alcohol thus obtained has a strong aromatic odour, a specific gravity of 0·819 at 23°, and boils at 156·6°. By oxidation it yields a caproic acid, $C_6H_{12}O_2$, having the same boiling point (204·5°), as normal caproic acid. The corresponding *iodide* is a heavy colourless liquid, boiling at 179·5°. The *acetate*, $C_6H_{13}.C_2H_3O_2$, has a pleasant fruity odour, and boils at 169°.

The same alcohol is obtained, together with butyl-methyl carbinol, by treating normal hexane, $CH_3.(CH_2)_4.CH_3$, from American petroleum with chlorine, converting the resulting hexyl chloride into the acetate by treatment with silver acetate, and distilling this acetate with potash. The mixture of alcohols thus obtained cannot be completely separated by fractional distillation, but it yields by oxidation the corresponding products, viz., normal caproic acid and methyl-butyl ketone.

Lastly, normal hexyl alcohol is obtained, according to Rossi, by the action of sodium-amalgam and water on normal caproic aldehyde.

Another primary hexyl alcohol, boiling at about 150°, and yielding caproic acid by oxidation, was found by Faget in fusel-oil. The statements respecting it are not very exact, but as it is produced, by fermentation, it is probably the isoprimary alcohol,



$$HC\left\{\begin{array}{l}C_3H_6OH\\CH_3\\CH_3\end{array}\right. .$$

Secondary Hexyl Alcohols.—1. *Methyl-butyl Carbinol*, $HO.HC{<}\begin{array}{l}C_4H_9\\CH_3\end{array}$, discovered by Wanklyn and Erlenmeyer, is produced by treating mannite, $C_6H_{14}O_6$ (a saccharine body obtained from manna), with a large excess of very strong hydriodic acid, whereby it is converted into secondary hexyl iodide:

$$C_6H_{14}O_6 + 11HI = C_6H_{13}I + 6H_2O + I_{10};$$

and digesting this compound with silver oxide and water:

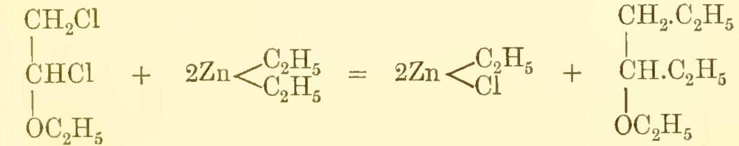
$$C_6H_{13}I + AgHO = AgI + C_6H_{14}O.$$

Methyl-butyl carbinol is a viscid liquid, having a pleasant, refreshing odour,; it boils at 137°; has a sp. gr. of 0·8327 at 0°, 0·8209 at 16°, and 0·7422 at 99°, so that it expands somewhat rapidly by heat. Strong hydrochloric acid converts it into the corresponding chloride, $ClHC{<}\begin{array}{l}C_4H_9\\CH_3\end{array}$, which boils at 120°, and yields hexene when digested at 100° with alcoholic potash. The iodide boils at 167–168°.

The alcohol is converted by oxidation with a mixture of potassium dichromate and sulphuric acid into methyl-butyl ketone, $CO\Big<^{C_4H_9}_{CH_3}$, which, when further treated with the oxidising mixture, yields acetic, carbonic, and normal butyric acids.

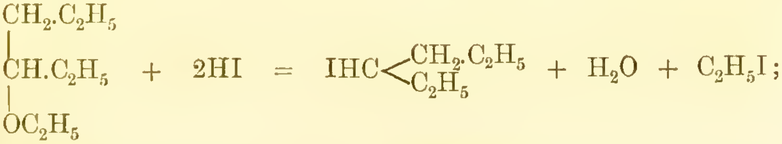
2. Methyl-katabutyl Carbinol, $HO.HC\Big<^{C(CH^3)^3}_{CH_3}$, also called *Pinacolyl alcohol,* is formed by the action of nascent hydrogen on pinacolin (*q.v.*). It solidifies at low temperatures to crystals which melt at +4°, boils at 120°, and has a specific gravity of 0·834. When oxidised by potassium dichromate and sulphuric acid, it is converted into methyl-katabutyl ketone, $CH_3—CO—C(CH_3)_3$, which splits up on further oxidation into carbon dioxide and trimethylacetic acid.

3. *Ethyl-propyl Carbinol,* $HO.HC\Big<^{CH_2CH_2CH_3}_{CH_2CH_3}$, also called *Hexene hydrate.*—The iodide analogous to this alcohol is prepared from dichlorethyl oxide, $O\Big<^{C_2H_3Cl_2}_{C_2H_5}$, by successive treatment with zinc-ethyl and hydriodic acid; thus:



$$\begin{array}{c}CH_2Cl\\|\\CHCl\\|\\OC_2H_5\end{array} + 2Zn\Big<^{C_2H_5}_{C_2H_5} = 2Zn\Big<^{C_2H_5}_{Cl} + \begin{array}{c}CH_2.C_2H_5\\|\\CH.C_2H_5\\|\\OC_2H_5\end{array}$$

Dichlorethyl oxide. Zinc-ethyl. Zinc-ethylo-chloride. Diethylated ethyl-oxide.



$$\begin{array}{c}CH_2.C_2H_5\\|\\CH.C_2H_5\\|\\OC_2H_5\end{array} + 2HI = IHC\Big<^{CH_2.C_2H_5}_{C_2H_5} + H_2O + C_2H_5I;$$

Diethylated ethyl oxide. Ethyl-propyl-carbinyl iodide.

and the alcohol is obtained by converting the iodide into the acetate, and distilling the latter with potash.

Tertiary Hexyl Alcohols.—Three of these alcohols are possible, and have been obtained, viz.:

Methyl-diethyl carbinol,	$C\left\{\begin{matrix}CH_3\\(C_2H_5)_2\\OH\end{matrix}\right.$	or $HO.C\left\{\begin{matrix}CH_3\\C_2H_5\\C_2H_5\end{matrix}\right.$
Propyl-dimethyl carbinol,	$C\left\{\begin{matrix}CH_2CH_2CH_3\\(CH_3)_2\\OH\end{matrix}\right.$	or $HO.C\left\{\begin{matrix}C_3H_7\\CH_3\\CH_3\end{matrix}\right.$
Isopropyl-dimethyl carbinol,	$C\left\{\begin{matrix}CH(CH_3)_2\\(CH_3)_2\\OH\end{matrix}\right.$	or $HO.C\left\{\begin{matrix}CH(CH_3)_2\\CH_3\\CH_3\end{matrix}\right.$

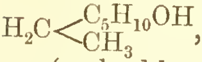
The first is prepared by treating acetyl chloride, $COCH_3Cl$, with zinc-ethyl, and decomposing the resulting methyl-diethyl-chloromethane, $C(CH_3)(C_2H_5)_2Cl$, with water. It boils at 120°, and yields by oxidation nothing but acetic acid.

The second, obtained in like manner from butyryl chloride, $CO(C_3H_7)Cl$, and zinc-methyl, boils at 115°, and is resolved by oxidation into acetic acid, propionic acid, and carbon dioxide.

The third, obtained from isobutyryl chloride and zinc-methyl, is a liquid which solidifies at $-35°$, boils at 112°, and yields by oxidation acetone, acetic acid, and carbon dioxide.

HEPTYL ALCOHOLS, $C_7H_{15}OH$.

Of these alcohols six have been obtained, two primary, one secondary, and three tertiary.

Normal Heptyl Alcohol, $CH_3(CH_2)_5.CH_2OH$, or  $H_2C{<}\begin{matrix}C_5H_{10}OH\\CH_3\end{matrix}$, is prepared, either by the action of nascent hydrogen (evolved by the action of sodium-amalgam on water), on heptyl aldehyde (œnanthol):

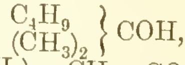
$$\underset{\text{Aldehyde.}}{C_7H_{14}O} + H_2 = \underset{\text{Alcohol.}}{C_7H_{16}O};$$

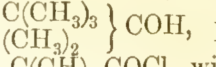
or from normal heptane, C_7H_{16}, in the same manner as normal hexyl alcohol from hexane (p. 154). It is a colourless, oily liquid, insoluble in water, boiling at 177°, and converted by oxidation into normal œnanthylic acid.

Another heptyl alcohol, probably the *isoprimary*, was separated by Faget from fusel-oil.

Secondary Heptyl Alcohol, or **Dipropyl Carbinol,** $C_3H_7—CHOH—C_3H_7$, prepared by hydrogenation of dipropyl ketone, boils at 150°, and is reconverted into the ketone by oxidation.

Tertiary Heptyl Alcohols.—*Triethyl Carbinol,* $(C_2H_5)_3COH$ is obtained by treating propionyl chloride, C_3H_5OCl, with zinc-methyl, and the product with water. It remains liquid at $-20°$, boils at 140°–142°, is slightly soluble in water, and has a specific gravity of 0·8593 at 0°. By oxidation with chromic acid it yields heptene, C_7H_{14}, together with carbon dioxide, and apparently also acetic and propionic acids.

Dimethyl-isobutyl Carbinol,  $\left.\begin{matrix}C_4H_9\\(CH_3)_2\end{matrix}\right\}COH$, obtained by treating isovaleric chloride, $CH(CH_3)_2—CH_2—COCl$, with zinc-methyl, and decomposing the product with water, boils at 129°–131°, and is converted by oxidation into acetic and isobutyric acids.

Dimethyl-katabutyl Carbinol, or *Pentamethylated Ethyl Alcohol,*  $\left.\begin{matrix}C(CH_3)_3\\(CH_3)_2\end{matrix}\right\}COH$, prepared by treating trimethyl-acetyl chloride, $C(CH)_3.COCl$, with zinc-methyl, and the product with water, melts at 17°, boils at 131°–132°, and forms with water a crystalline hydrate, $2C_7H_{16}O.H_2O$, which melts at 83°.

OCTYL ALCOHOLS, $C_8H_{17}OH$.

Five of these alcohols are known—one primary, three secondary, and one tertiary.

Primary Octyl Alcohol or Heptyl Carbinol, $C_7H_{15}.CH_2OH$, is contained, together with the corresponding acetate, $C_8H_{17}.C_2H_3O_2$, in the volatile oil obtained from the seed of the cow-parsnep (*Heracleum sphondylium*); also as a butyric ether in the seeds of the common parsnep (*Pastinaca sativa*); and, together with hexyl butyrate, in the oil of *Heracleum giganteum.*

The comparatively small portion of cow-parsnep oil, which boils between 190° and 195°, consists mainly of the alcohol; but by far the greater portion passes over between 200° and 212°, and this, by continued fractionation, yields primary octyl acetate, $C_{10}H_{20}O_2$, boiling between 206° and 208°. This compound is insoluble in water, easily soluble in alcohol and ether, and has a sp. gr. of 0·8717 at 16°. Heated with alcoholic potash, it yields potassium acetate and primary octyl alcohol.

This alcohol is a colourless oily liquid, having a sp. gr. of 0·830 at 16°, boiling between 190° and 192°, nearly insoluble in water, miscible with alcohol and ether; it has a peculiarly pungent aromatic odour, and tastes sweetish at first, afterwards burning and sharp. By boiling with potassium dichromate and dilute sulphuric acid, it is converted into an acid, $C_8H_{16}O_2$, melting at 16° to 17°, and isomeric or identical with the caprylic acid of natural fats, together with the corresponding octylic ether, $C_8H_{17}.C_8H_{15}O_2$. This reaction shows it to be a primary alcohol; and from the boiling point of the octane obtained from it (122°–125°),* Schorlemmer infers that it is an iso-alcohol, $HC\left\{\begin{array}{l}C_5H_{10}OH\\(CH_3)_2\end{array}\right.$

The haloïd octyl ethers obtained from this alcohol exhibit the following properties:

	Boiling Point.	Sp. gr.
Chloride, $C_8H_{17}Cl$,	179·5°–180°	0·8802 at 16°
Bromide, $C_8H_{17}Br$, .	198°—200°	1·1116 ”
Iodide, $C_8H_{17}I$, .	220°—222°	1·1338 ”

Primary octyl alcohols, convertible by oxidation into caprylic acids, are also obtained from octane; they differ from the alcohol obtained from heracleum oil, but their exact structure has not been ascertained.

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* Normal pentane, C_5H_{12}, boils at 38°, and the average difference of boiling point between any two consecutive members of the normal paraffin series is about 31° (p. 50): hence the boiling point of normal octane should be 38 + 3 × 31 = 131°. On the other hand, isopentane boils at 30°, and the difference of boiling point between two consecutive isoparaffins is also about 31°: hence the boiling point of iso-octane should be 30 + 3 × 31 = 123°. (Schorlemmer, Proceedings of the Royal Society, xvi. 376; see also Watts's Dictionary of Chemistry, First Supplement, p. 879.

Secondary Octyl Alcohols.—1. *Methyl-hexyl Carbinol*, $HO.HC\left\{\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\right.$, is produced by heating castor oil with excess of solid potassium hydroxide. Castor oil contains ricinolcic acid, $C_{18}H_{34}O_3$, and this acid, when heated with potash, yields free hydrogen, a distillate containing methyl-hexyl carbinol, together with products of its decomposition, and a residue of potassium sebate, $C_{10}H_{16}K_2O_4$:

$$C_{18}H_{34}O_3 + 2KOH = C_8H_{18}O + C_{10}H_{16}K_2O_4 + H_2.$$

To separate the alcohol, the distillate is repeatedly rectified over fused potash, the portion boiling below 200° only being collected: this liquid, subjected to fractional distillation, yields a portion boiling at 181°, which is the pure secondary octyl alcohol. The portions of the original distillate having a lower boiling point, consist of olefines, amongst which octene, C_8H_{16}, boiling at 150°, preponderates.

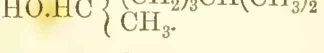
The same alcohol is obtained from the octane of American petroleum, by converting this hydrocarbon into octyl chloride, then into the acetate, and heating the latter with alcoholic potash.

Methyl-hexyl carbinol is a limpid oily liquid, having a strong aromatic odour, and making grease-spots on paper. It has no action on polarised light. It has a specific gravity of 0·823 at 17°, and boils at 181°. It is insoluble in water, but dissolves in alcohol, ether, wood-spirit, and acetic acid. It mixes with sulphuric acid, forming octyl-sulphuric acid, $C_8H_{17}HSO_4$, generally also octene and neutral octyl sulphate. Fused zinc chloride converts it into octene. With potassium and sodium it yields substitution-products.

Methyl-hexyl carbinol, oxidised with potassium dichromate and sulphuric acid, yields the corresponding ketone, viz., methyl-hexyl ketone, $CH_3—CO—C_6H_{13}$, and by the prolonged action of the oxidising mixture, this ketone is further oxidised to caproic and acetic acids:

$$C_8H_{18}O + O_4 = C_6H_{12}O_2 + C_2H_4O_2 + H_2O.$$

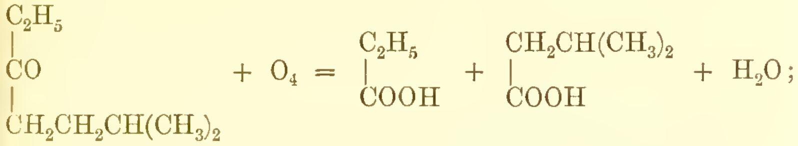
These reactions show that the alcohol produced from castor oil is a secondary alcohol; and from considerations similar to those above adduced with respect to the primary alcohol, it is inferred to be a secondary iso-alcohol, represented by the formula:



$$HO.HC\left\{\begin{matrix}(CH_2)_3CH(CH_3)_2\\CH_3.\end{matrix}\right.$$

The chloride, $C_8H_{17}Cl$, produced by the action of phosphorus pentachloride on this alcohol, has an odour of oranges, a specific gravity of 0·892 at 18°, and boils at 175°. Heated with alcoholic potash, it yields octene, C_8H_{16}; by alcohol and potassium acetate, it is converted into octene and octyl acetate.

2. *Ethyl-isopentyl Carbinol*, $HO.CH\left\{\begin{matrix}CH_2CH_3\\(CH_2)_2CH(CH_3)_2\end{matrix}\right.$, is obtained together with the primary alcohol, from the octane produced by the action of zinc and hydrochloric acid on the secondary octyl iodide obtained from the alcohol last described. The octyl chloride prepared from this octane smells faintly of oranges, and the acetate prepared from it yields, when heated with alcoholic potash, an octyl alcohol, which boils at 182°–186°, and is converted by oxidation into a ketone, $C_8H_{16}O$, isomeric with methyl-hexyl ketone, but differing from it by yielding when further oxidised, not caproic and acetic, but propionic and ordinary valeric acid : hence it consists of ethyl-isopentyl ketone (see KETONES) :



$$\begin{matrix}C_2H_5\\|\\CO\\|\\CH_2CH_2CH(CH_3)_2\end{matrix} + O_4 = \begin{matrix}C_2H_5\\|\\COOH\end{matrix} + \begin{matrix}CH_2CH(CH_3)_2\\|\\COOH\end{matrix} + H_2O;$$

Ethyl-isopentyl ketone. Propionic acid. Valeric acid.

and the alcohol from which it is obtained is ethyl-isopentyl carbinol.

3. A secondary octyl alcohol, different from both the preceding, has been obtained from octene, by heating this hydrocarbon in a sealed tube with hydriodic acid, converting the resulting octyl iodide, or octene hydriodide, $C_8H_{16}.HI$, into the acetate, and distilling the latter with finely pulverised potassium hydroxide. This alcohol has an aromatic odour, a specific gravity of 0·811 at 0°, and boils at 174°–178°. By oxidation it yields the same products as the castor oil alcohol, and must therefore likewise consist of methyl-hexyl carbinol; but as it boils at a lower temperature than the latter, it probably contains a different modification of hexyl.

Tertiary Octyl Alcohol, or **Propyl-diethyl Carbinol,** $HO.C\left\{\begin{matrix}C_3H_7\\C_2H_5\\C_2H_5\end{matrix}\right.$, is formed by treating butyryl chloride, C_3H_7COCl, with zinc-ethyl, and decomposing the product with water. It is a somewhat viscid liquid, lighter than water, and insoluble therein, and does not solidify in a freezing mixture. With phosphorus pentachloride it yields an octyl chloride boiling at 155°. By oxidation with chromic acid mixture it yields propionic and acetic acids.

Nonyl Alcohol, $C_9H_{19}OH$, is obtained by the series of reactions above described from the nonane of American petroleum, and likewise occurs, together with nonene, C_9H_{18}, in that portion of the liquid obtained by distilling amyl alcohol with zinc chloride, which boils between 134° and 150°. Nonyl alcohol boils at about 200°. Nonyl chloride, $C_9H_{19}Cl$, has a specific gravity of 0·899 at 16°, and boils at 196°.

Decyl Alcohol, $C_{10}H_{21}OH$, from petroleum decane, boils at 210°–215°. An isomeric alcohol, probably tetra-ethylated ethyl alcohol, $CH(C_2H_5)_2—C(C_2H_5)_2OH$, is formed by the action of dibromacetyl bromide, $CHBr.COBr$, on zinc-ethyl; it boils at 155°–157°.

The alcohols of the series $C_nH_{2n+2}O$ containing 11 to 15 carbon-atoms, are not known, but compound ethers containing 12 and 14 carbon-atoms appear to occur in spermaceti.

Hexdecyl or **Cetyl Alcohol**, $C_{16}H_{34}O = C_{16}H_{33}(OH)$, also called *Ethal*, is obtained from spermaceti, a crystalline fatty substance found in peculiar cavities in the head of the sperm whale (*Physetcr macrocephalus*). This substance consists of cetyl palmitate, $C_{32}H_{64}O_2$, or $C_{16}H_{33}.C_{16}H_{31}O_2$, and when heated for some time with solid potash, is resolved into potassium palmitate and cetyl alcohol:

$$C_{16}H_{33}.C_{16}H_{31}O_2 + KOH = KC_{16}H_{31}O_2 + C_{16}H_{33}(OH) .$$

The cetyl alcohol is dissolved out from the fused mass by alcohol and ether, and purified by several crystallisations from ether.

Cetyl alcohol, or ethal, is a white crystalline mass, which melts at about 50°, and crystallises by slowly cooling in shining laminæ. It has neither taste nor smell, is insoluble in water, but dissolves in all proportions in alcohol and ether. When heated it distils without decomposition. With sodium it gives off hydrogen and yields sodium cetylate, $C_{16}H_{33}NaO$. It is not dissolved by aqueous alkalis; but when heated with a mixture of potash and lime, it gives off hydrogen, and is converted into palmitic acid:

$$C_{10}H_{34}O + KOH = KC_{16}H_{31}O_2 + 2H_2 .$$

Distilled with phosphorus pentachloride it yields cetyl chloride, $C_{16}H_{33}Cl$, a limpid oily liquid, having a specific gravity of 0·8412 at 12°, and distilling with partial decomposition at a temperature above 200°. Cetyl iodide, $C_{16}H_{33}I$, obtained by treating the alcohol with iodine and phosphorus, is a solid substance which melts at 22°, dissolves in alcohol and ether, and crystallises from alcohol in interlaced laminæ.

According to Heintz, cetyl alcohol, or ethal, prepared as above, is not a definite compound, but a mixture of hexdecyl alcohol, $C_{16}H_{34}O_2$, with small quantities of three other alcohols of the same series, containing respectively 12, 14, and 18 atoms of carbon, inasmuch as, when fused with potash-lime, it yields the corresponding fatty acids, $C_nH_{2n}O_2$.

Ceryl Alcohol, $C_{27}H_{56}O = C_{27}H_{55}(OH)$; also called *Cerotic alcohol* and *Cerotin*.—This alcohol is obtained from Chinese wax or Pela, a secretion enveloping the branches of certain trees in China, and supposed to be produced by the puncture of an insect. This wax consists mainly of ceryl cerotate, $C_{27}H_{55}.C_{27}H_{53}O_2$, and is decomposed by fused potash in the same manner as spermaceti, yielding potassium cerotate and ceryl alcohol:

$$C_{27}H_{55}.C_{27}H_{53}O_2 + KOH = KC_{27}H_{53}O_2 + C_{27}H_{55}(OH).$$

On digesting the fused mass with boiling water, a solution of potassium cerotate is obtained, holding ceryl alcohol in suspension; and on precipitating the cerotic acid with barium chloride, and treating the resulting precipitate with alcohol, the ceryl alcohol dissolves, and may be purified by repeated crystallisation from alcohol or ether. It then forms a waxy substance, melting at 97°. Heated with potash-lime, it gives off hydrogen, and is converted into potassium cerotate. At very high temperatures it distils, partly undecomposed, partly resolved into water and cerotene, $C_{27}H_{54}$; by this character it would appear to be related to the secondary alcohols. With sulphuric acid in excess, it forms hydrated neutral ceryl sulphate, $(C_{27}H_{55})_2SO_4.H_2O$.

Myricyl Alcohol, $C_{30}H_{62}O = C_{30}H_{61}(OH)$.—This alcohol, the highest known member of the series, $C_nH_{2n+2}O$, is obtained from myricin, the portion of common bees' wax which is insoluble in boiling alcohol. Myricin consists of myricyl palmitate, $C_{30}H_{61}.C_{16}H_{31}O_2$, and when heated with potash is decomposed in the same manner as spermaceti and Chinese wax, yielding potassium palmitate and myricyl alcohol. On dissolving the product in water, precipitating with barium chloride, exhausting the precipitate with boiling alcohol, and dissolving the substance deposited from the alcohol in light petroleum, pure myricyl alcohol separates as a crystalline substance, having a silky lustre. When heated, it partly sublimes unaltered, and is partly resolved (like ceryl alcohol) into water and melene, $C_{30}H_{60}$. With strong *sulphuric acid* it yields myricyl sulphate. Heated with *potash-lime*, it gives off hydrogen, and is converted into potassium melissate:

$$C_{30}H_{62}O + KOH = KC_{30}H_{59}O_2 + 2H_2.$$

The mother-liquor from which the myricyl alcohol has crystallised out, as above mentioned, retains a small quantity of an isomeric alcohol, which melts at 72°, and when treated with potash-lime yields an acid containing a smaller proportion of carbon.

2. Monatomic Alcohols, $C_nH_{2n}O$, or $C_nH_{2n-1}OH$.

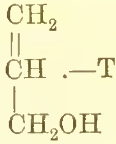
Two alcohols of this series are known, viz.:

$$\text{Vinyl alcohol, } C_2H_4O = C_2H_3(OH)$$
$$\text{Allyl alcohol, } C_3H_6O = C_3H_5(OH).$$

The first, discovered by Berthelot in 1860, is produced by combining ethine or acetylene with sulphuric acid, whereby vinyl sulphuric acid $(C_2H_3)HSO_4$ is formed, and distilling the product with water, just as in the preparation of ethyl alcohol from ethene:

$$HHSO_4 + C_2H_2 = (C_2H_3)HSO_4$$
$$(C_2H_3)HSO_4 + HOH = HHSO_4 + C_2H_3(OH).$$

It is an easily decomposible liquid, having a highly pungent odour, somewhat more volatile than water, soluble in 10 to 15 parts of that liquid, and precipitated from the solution by potassium carbonate. It is isomeric with acetic aldehyde and ethene oxide (p. 170). The univalent radicle vinyl, C_2H_3, which may be supposed to exist in it, is related to the trivalent radicle ethenyl (p. 23) in the same manner as allyl to propenyl (see below).



Allyl Alcohol, $C_3H_6O = C_3H_5(OH) = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}$.—This alcohol, discovered by Cahours and Hofmann in 1856, may be supposed to contain the univalent radicle allyl, C_3H_5, derived from a saturated hydrocarbon by abstraction of one atom of hydrogen, and isomeric with the trivalent radicle propenyl, (C_3H_5), derived from propane, $CH_3—CH_2—CH_3$, by abstraction of three atoms of hydrogen. Allyl and propenyl compounds, indeed, are easily converted one into the other by addition or subtraction of two atoms of a monad element or radicle.

To obtain the alcohol, allyl iodide is first prepared by the action of phosphorus tetriodide on propenyl alcohol (glycerin), $(C_3H_5)(OH)_3$:

$$2(C_3H_5)(OH)_3 + P_2I_4 = 2C_3H_5I + 2P(OH)_3 + I_2.$$

The allyl iodide is next decomposed by silver oxalate, yielding allyl oxalate:

$$2C_3H_5I + Ag_2C_2O_4 = 2AgI + (C_3H_5)_2C_2O_4;$$

and the allyl oxalate is decomposed by ammonia, yielding oxamide, $C_2O_2(NH_2)_2$, and allyl alcohol:

$$(C_3H_5)_2C_2O_4 + 2NH_3 = (C_2O_2)(NH_2)_2 + 2C_3H_5(OH).$$

Allyl alcohol is a colourless liquid, having a pungent odour and a spirituous burning taste. It mixes in all proportions with water, common alcohol, and ether; boils at 103°; burns with a brighter flame than common alcohol.

Allyl alcohol is a primary alcohol, similar in all its ordinary reactions to ethyl alcohol. By oxidation in contact with platinum black, or more quickly by treatment with potassium dichromate and sulphuric acid, it is converted into acrylic aldehyde (acrolein), C_3H_4O, and acrylic acid, $C_3H_4O_2$, compounds related to it in the same manner as common aldehyde and acetic acid to ethyl alcohol. Heated with phosphoric oxide, it yields allylene, C_3H_4. With potassium and sodium it yields substitution-products. Strong sulphuric acid converts it into allyl-sulphuric acid. With the bromides and chlorides of phosphorus it yields allyl bromide, C_3H_5Br, and allyl chloride, C_3H_5Cl.

ALLYL BROMIDES.—The *monobromide*, C_3H_5Br, prepared as just mentioned, or by distilling propene bromide, $C_3H_6Br_2$, with alcoholic potash, is a liquid of specific gravity 1·47, and boiling at 62°. A *tribromide of allyl*, $C_3H_5Br_3$, is obtained by adding bromine to the mono-iodide in a vessel surrounded by a freezing mixture. It is a liquid of specific gravity 1·436 at 23°, boiling at 217°, and solidifying when cooled below 10°. It is isomeric with propenyl bromide or tribromhydrin, obtained by the action of phosphorus pentabromide on glycerin.

A *diallyl tetrabromide*, $C_6H_{10}Br_4$, is formed by the direct combination of diallyl (p. 64), with bromine; it is a crystalline body, melting at 37°.

ALLYL IODIDES,—The *mono-iodide*, C_3H_5I, obtained, as above described, by distilling glycerin with phosphorus tetriodide, is a liquid of specific gravity 1·780 at 160°, and boiling at 100°. It is decomposed by sodium, with formation of diallyl, C_6H_{10}. By the action of zinc or mercury and hydrochloric or dilute sulphuric acid, it is converted into propene (or allyl hydride):

$$2C_3H_5I + Zn_2 + 2HCl = ZnCl_2 + ZnI_2 + 2C_3H_6.$$

Diallyl tetriodide, $C_6H_{10}I_4$, is a crystalline body obtained by dissolving iodine in diallyl at a gentle heat.

ALLYL-SULPHURIC ACID, $(C_3H_5)HSO_4$, is produced by adding allyl alcohol to strong sulphuric acid. The solution, diluted with water and neutralised with barium carbonate, yields barium allylsulphate, $(C_3H_5)_2Ba(SO_4)_2$.

ALLYL OXIDE, $(C_3H_5)_2O$, is produced by the action of allyl iodide on potassium allylate (the gelatinous mass obtained by dissolving potassium in allyl alcohol):

$$C_3H_5OK + C_3H_5I = KI + (C_3H_5)_2O.$$

It is a colourless liquid, boiling at 82°.

ALLYL SULPHIDE, $(C_3H_5)_2S$.—This compound exists, together with a small quantity of allyl oxide, in volatile oil of garlic, and is formed artificially by distilling allyl iodide with potassium monosulphide:

$$2C_3H_5I + K_2S = 2KI + (C_3H_5)_2S.$$

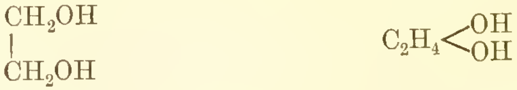
To prepare it from garlic, the sliced bulbs are distilled with water, and the crude oil thus obtained—which is a mixture of the sulphide and oxide of allyl—is subjected to the action of metallic potassium, renewed until it is no longer tarnished, whereby the allyl oxide is decomposed, after which the sulphide may be obtained pure by redistillation. In this state it forms a colourless liquid, lighter than water, of high refractive power, possessing in a high degree the peculiar odour of the plant, and distilling without decomposition. Allyl sulphide, dissolved in alcohol and mixed with solutions of platinum, silver, and mercury, gives rise to crystalline compounds, consisting of a double sulphide of allyl and the metal, either alone or mixed with a double chloride.

Volatile Oil of Mustard, consisting essentially of allyl isothiocyanate, $C_3H_5.CNS$, is described in connection with the thiocyanic ethers (p. 104).

Allyl Hydrosulphide, or *Allyl Mercaptan*, $C_3H_5(SH)$, obtained by distilling allyl iodide with potassium hydrosulphide, is a volatile oily liquid, having an odour like that of garlic oil, but more ethereal, boiling at 90°. It attacks mercuric oxide like ethyl mercaptan, forming the compound $Hg(C_3H_5)_2S_2$.

DIATOMIC ALCOHOLS AND ETHERS.

The diatomic alcohols are derived from saturated hydrocarbons by substitution of two equivalents of hydroxyl for two atoms of hydrogen, and may therefore be regarded as compounds of bivalent radicles with two equivalents of hydroxyl: ethene alcohol, for example, may be represented by either of the formulæ:



$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} \qquad\qquad C_2H_4<\begin{matrix}OH\\OH\end{matrix}$$

the first representing it as a derivative of ethane, $\begin{matrix}CH_3\\|\\CH_3\end{matrix}$; the second as a compound of ethene, C_2H_4, with hydroxyl, or as derived from a double molecule of water, $H_2(OH)_2$, by substitution of ethene for two atoms of hydrogen.

The diatomic alcohols of the fatty group, called glycols, are represented by the general formula,

$$C_nH_{2n+2}O_2 \text{ or } (C_nH_{2n})(OH)_2 .$$

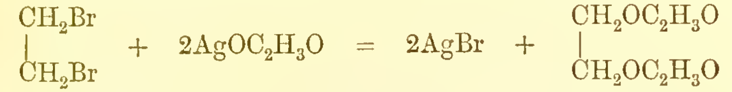
They may be regarded as compounds of olefines with two equivalents of hydroxyl. The following are known:

Ethene alcohol, . .	$C_2H_6O_2$	$= C_2H_4(OH)_2$
Propene alcohol, . .	$C_3H_8O_2$	$= C_3H_6(OH)_2$
Tetrene or Butene alcohol, .	$C_4H_{10}O_2$	$= C_4H_8(OH)_2$
Pentene or Amylene alcohol,	$C_5H_{12}O_2$	$= C_5H_{10}(OH)_2$
Octene alcohol, . .	$C_8H_{18}O_2$	$= C_8H_{16}(OH)_2$

The glycols are formed by the following processes:

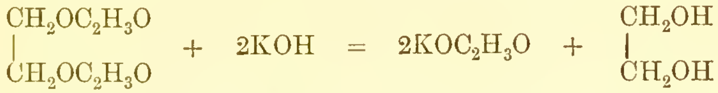
1. By combining an olefine with bromine; treating the result-

ing dibromide with an alcoholic solution of potassium acetate, or with silver acetate, whereby it is converted into a diacetate of the olefine; and decomposing this compound with solid potassium hydroxide, whereby potassium acetate and a diatomic alcohol are formed, the latter of which may be distilled off:



$$\begin{array}{l}\mathrm{CH_2Br}\\ |\\ \mathrm{CH_2Br}\end{array} + \mathrm{2AgOC_2H_3O} = \mathrm{2AgBr} + \begin{array}{l}\mathrm{CH_2OC_2H_3O}\\ |\\ \mathrm{CH_2OC_2H_3O}\end{array}$$

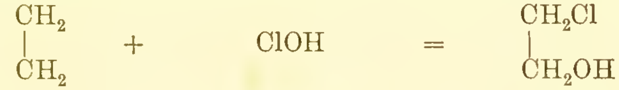
Ethene bromide. Silver acetate. Ethene diacetate.



$$\begin{array}{l}\mathrm{CH_2OC_2H_3O}\\ |\\ \mathrm{CH_2OC_2H_3O}\end{array} + \mathrm{2KOH} = \mathrm{2KOC_2H_3O} + \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

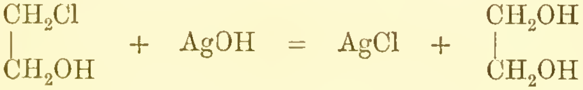
Ethene diacetate. Potassium hydroxide. Potassium acetate. Ethene alcohol.

2. By combining an olefine with hypochlorous acid, and treating the resulting compound (a chlorhydrin) with moist silver oxide:



$$\begin{array}{l}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{array} + \mathrm{ClOH} = \begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Ethene. Ethene chlorhydrin.

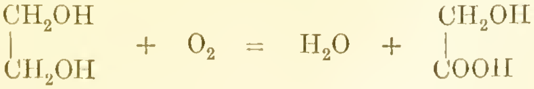


$$\begin{array}{l}\mathrm{CH_2Cl}\\ |\\ \mathrm{CH_2OH}\end{array} + \mathrm{AgOH} = \mathrm{AgCl} + \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

Properties.—The glycols are colourless, inodorous, more or less viscid liquids, having a sweetish taste, freely soluble in water and alcohol; ethene alcohol is but sparingly soluble in ether; the rest dissolve easily in that liquid.

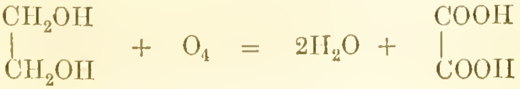
The chemical reactions of the glycols have been studied chiefly in the case of ethene alcohol. They are, for the most part, similar to those of the monatomic alcohols; but inasmuch as the glycols contain two atoms of replaceable hydrogen, or of hydroxyl, the reactions generally take place by two stages, yielding two series of products.

1. Ethene alcohol treated with *nitric acid* gives up 2 or 4 atoms of hydrogen in exchange for oxygen, and is converted into glycollic acid, $C_2H_4O_3$, or oxalic acid, $C_2H_2O_4$, according as the action takes place at ordinary or at higher temperatures; thus:



$$\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{array} + \mathrm{O_2} = \mathrm{H_2O} + \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{COOH}\end{array}$$

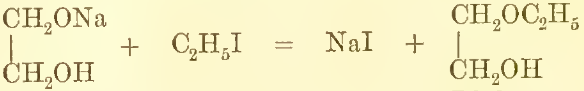
and



$$\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{array} + \mathrm{O_4} = \mathrm{2H_2O} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

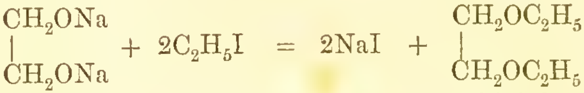
Under certain circumstances the corresponding aldehydes are also produced, as glyoxal, $\begin{array}{l}COH\\ |\\ COH\end{array}$, from ethene alcohol, by removal of four hydrogen-atoms without substitution.

2 *Potassium* and *sodium* eliminate one or two atoms of hydrogen from the glycols, and form substitution-products. Ethene alcohol is strongly attacked by sodium, yielding sodium ethenate, $C_2H_5NaO_2$; and this compound, fused with excess of sodium, is converted into disodium ethenate, $C_2H_4Na_2O_2$. These compounds, treated with monatomic alcoholic iodides, yield the alcoholic ethers of the glycols; thus:



$$\begin{array}{l}CH_2ONa\\ |\\ CH_2OH\end{array} + C_2H_5I = NaI + \begin{array}{l}CH_2OC_2H_5\\ |\\ CH_2OH\end{array}$$

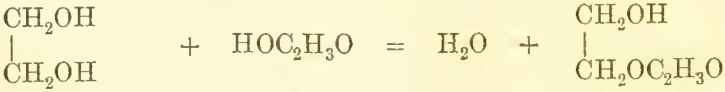
Sodium ethenate. Ethyl ethenate.



$$\begin{array}{l}CH_2ONa\\ |\\ CH_2ONa\end{array} + 2C_2H_5I = 2NaI + \begin{array}{l}CH_2OC_2H_5\\ |\\ CH_2OC_2H_5\end{array}$$

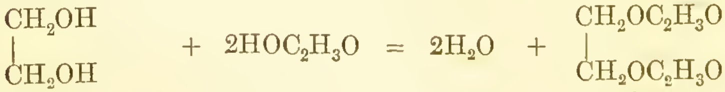
Disodium ethenate. Diethyl ethenate.

3. *Oxygen acids*, heated with glycols in closed vessels, act upon them in the same manner as upon the monatomic alcohols, converting them into ethereal salts or compound ethers, mono-acid or di-acid, according to the proportions used. In the di-acid glycol-ethers, the two radicles by which the hydrogen is replaced may belong either to the same or to different acids; *e g.*,



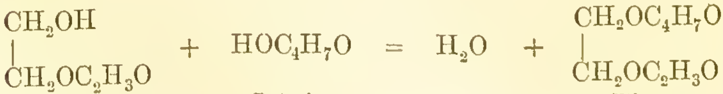
$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + HOC_2H_3O = H_2O + \begin{array}{l}CH_2OH\\ |\\ CH_2OC_2H_3O\end{array}$$

Ethene alcohol. Acetic acid. Ethene mono-acetate.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + 2HOC_2H_3O = 2H_2O + \begin{array}{l}CH_2OC_2H_3O\\ |\\ CH_2OC_2H_3O\end{array}$$

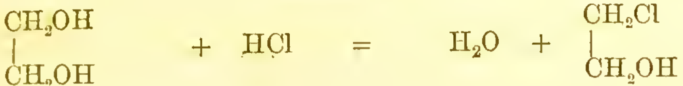
Ethene alcohol. Acetic acid. Ethene diacetate.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OC_2H_3O\end{array} + HOC_4H_7O = H_2O + \begin{array}{l}CH_2OC_4H_7O\\ |\\ CH_2OC_2H_3O\end{array}$$

Ethene mono-acetate. Butyric acid. Ethene butyracetate.

The *haloïd acids* (HCl and HBr), act in the same manner as oxygen-acids, excepting that the reaction never goes beyond the first stage; *e.g.*,



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + HCl = H_2O + \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array}$$

Ethene alcohol. Ethene chlorhydrin.

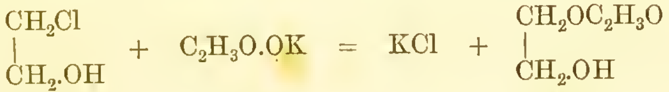
With *hydriodic acid*, a further action generally takes place, resulting in the separation of iodine, and the formation of an olefine: thus:

$$CH_2I—CH_2OH + IH = C_2H_4 + H_2O + I_2.$$

The monochlorhydrins, &c., of the glycols (haloïd hydrins), are also produced, as above mentioned, by direct addition of hypochlorous acid to the olefines. When treated with nascent hydrogen, they are converted into monatomic alcohols; *e.g.*,

$$C_2H_4Cl(OH) + H_2 = HCl + C_2H_5(OH).$$

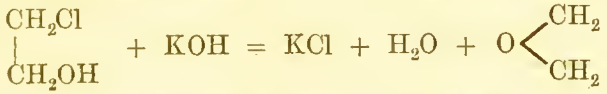
When heated with metallic salts they form mono-acid compound ethers:



$$\begin{array}{l}CH_2Cl\\ |\\ CH_2.OH\end{array} + C_2H_3O.OK = KCl + \begin{array}{l}CH_2OC_2H_3O\\ |\\ CH_2.OH\end{array}$$

Ethene chlorhydrin. Potassium acetate. Ethene monoacetate.

The haloïd hydrins treated with alkalis are converted into the oxygen-ethers or anhydrides of the glycols, $C_nH_{2n}O$; thus:



$$\begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} + KOH = KCl + H_2O + O\left<\begin{array}{l}CH_2\\ CH_2\end{array}\right.$$

These oxides are isomeric with the aldehydes and ketones.

The dichlorinated ethers, &c. (haloïd dihydrins), produced, as already observed, by direct combination of chlorine, bromine, and iodine, with the olefines (p. 68), may also be formed by the action of the chlorides, bromides, and iodides of phosphorus on the glycols; *e.g.*,

$$C_2H_4(OH)_2 + 2PCl_5 = 2POCl_3 + 2HCl + C_2H_4Cl_2.$$

Methene Glycol, $CH_2(OH)_2$ is not known, and in all probability cannot exist. It appears indeed that a single carbon-atom is not capable of attracting to itself more than one hydroxyl group; and in reactions, where such dihydroxyl-compounds might be expected to arise, water is separated, and the corresponding oxides (*i.e.*, aldehydes) are actually produced. Thus, on heating ethidene dichloride, $CH_3—CHCl_2$, with silver acetate, and distilling the resulting acetic ether with potash, the product obtained is not ethidene glycol, $CH_3—CH(OH)_2$, but the products of its decomposition, namely, water and aldehyde, $CH_3—CHO$.

Ethers of methene, or of methene-glycol, have however been produced. The haloïd ethers, CH_2I_2, &c., have been already described (p. 68).

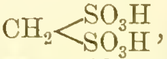
Methene Dimethylate, $CH_2(OCH_3)_2$, also called *Methylal* and *Formal*, is formed by the oxidation of methyl alcohol with manganese dioxide and sulphuric acid. It is an ethereal liquid, having a specific gravity of 0·855, and boiling at 42°. It mixes readily with alcohol and ether, and dissolves in three parts of water.

Methene Diacetate, $CH_2(OC_2H_3O)_2$, formed by the action of methene iodide on silver acetate, in an oily liquid, heavier than water, and boiling at 170°. It is insoluble in water, and when boiled with alkalis, is converted into methene oxide.

Methene Oxide, CH_2O, isomeric with formic aldehyde, H.CHO, is produced by the action of oxide or of oxalate of silver on methene iodide, in the latter case with evolution of carbon monoxide and dioxide :

$$CH_2I_2 + C_2O_4Ag_2 = CH_2O + CO_2 + CO + 2AgI.$$

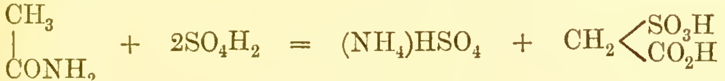
The distillate, however, consists, not of CH_2O, but of the polymeric compound, $C_3H_6O_3$, which collects in the receiver as a crystalline mass, soluble in water, alcohol, and ether, melting at 152°, and subliming below 100°. The density of its vapour is 1·06 referred to air, or 15 referred to hydrogen as unity; and as this is half the molecular weight represented by the formula CH_2O $(12+2+16=30)$, it follows that this formula correctly represents the molecule of the compound in the state of vapour. On the other hand, the solid compound, when treated with hydrogen sulphide, is converted into methene sulphide, a body which melts at 218°, sublimes easily, and yields a vapour whose density (69 referred to hydrogen), shows that the molecule of this compound is not CH_2S, but $C_3H_6S_3$. $\left(\frac{36+6+96}{2}=69\right)$. Hence it is inferred that the oxide from which it is formed has also, in the solid state, the constitution represented by the formula $C_3H_6O_3$, or $(CH_2)_3O_3$.



Methene-disulphonic or **Methionic acid,** $CH_2{<}\begin{smallmatrix}SO_3H\\SO_3H\end{smallmatrix}$, formed by the action of fuming sulphuric acid on acetamide or acetonitril (methyl cyanide, $CH_3.CN$; p. 169), crystallises in long deliquescent needles. It is very stable, not being altered by boiling with nitric acid. The barium-salt, $CH_2(SO_3)_2Ba + 2H_2O$, forms nacreous laminæ, sparingly soluble in water; it is precipitated from the aqueous solution of the acid by barium chloride.

Methene-hydrinsulphonic acid, $CH_2{<}\begin{smallmatrix}OH\\SO_3H\end{smallmatrix}$, or *Oxymethylsulphonic acid*, is obtained by acting on methyl alcohol with sulphuric anhydride, and boiling the product with water. It crystallises with difficulty, and is moderately stable. Its barium salt crystallises in small anhydrous tables.

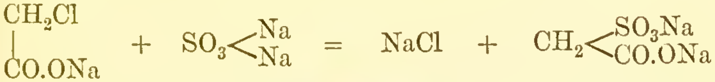
Sulphacetic acid, $CH_2<\begin{array}{l}SO_3H\\ CO_2H\end{array}$ (Methene carbonyl-sulphonic acid), is the first product of the action of sulphuric acid on acetamide or acetonitril:



$$\begin{array}{l}CH_3\\ |\\ CONH_2\end{array} + 2SO_4H_2 = (NH_4)HSO_4 + CH_2<\begin{array}{l}SO_3H\\ CO_2H\end{array}$$

Acetamide. Acid ammonium sulphate. Sulphacetic acid.

It is also produced by heating a mixture of glacial acetic acid and sulphuric anhydride, and as a sodium salt by boiling a solution of sodium sulphite with sodium monochloracetate:



$$\begin{array}{l}CH_2Cl\\ |\\ CO.ONa\end{array} + SO_3<\begin{array}{l}Na\\ Na\end{array} = NaCl + CH_2<\begin{array}{l}SO_3Na\\ CO.ONa\end{array}$$

By neutralising the solution obtained by the second process with lead carbonate, and decomposing the solution of the resulting lead-salt with hydrogen sulphide, a solution is obtained which, when concentrated, yields sulphacetic acid in transparent prisms.

Sulphacetic acid is a strong bibasic acid. When heated with sulphuric anhydride, it is converted into methene-disulphonic or methionic acid:

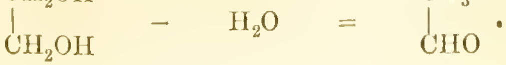
$$CH_2(SO_3H).CO_2H + SO_3 = CH_2(SO_3H)_2 + CO_2.$$

Hence, also, methionic acid is obtained as the ultimate product of the action of fuming sulphuric acid on acetamide or acetonitril.

Ethene Glycol, $C_2H_6O_2 = C_2H_4(OH)_2 = \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$, prepared by distilling the monoacetate or diacetate of ethene with caustic potash, is a colourless viscid liquid, having a specific gravity of 1·125 at 0°, and boiling at 197·5°. It mixes freely with water and alcohol, but is only slightly soluble in ether. Its reaction with sodium, and the formation of ethylic ethers by treating the resulting sodium derivatives with ethyl iodide, have been already described (pp. 166, 167).

Ethylic Ethenate, $C_2H_4(OH)(OC_2H_5)$, likewise formed by direct combination of ethene oxide with ethyl alcohol, is a liquid having a fragrant odour, and boiling at 127°. The *diethylic ether*, $C_2H_4(OC_2H_5)_2$, boils at 123°.

Glycol heated with *zinc chloride* yields aldehyde:



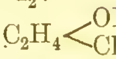
$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} - H_2O = \begin{array}{l}CH_3\\ |\\ CHO\end{array}.$$

With *phosphorus pentachloride* it forms ethene dichloride:

$$C_2H_4(OH)_2 + PCl_5 = PCl_3O + H_2O + C_2H_4Cl_2.$$

Hydriodic acid reduces it to ethyl iodide:

$$C_2H_4(OH)_2 + 3HI = C_2H_5I + 2H_2O + I_2.$$

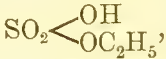


Ethene Chlorhydrate or **Ethene Chlorhydrin,** $C_2H_4{<}\begin{smallmatrix}OH\\Cl\end{smallmatrix}$, is formed by heating glycol with hydrochloric acid, or by agitating ethene with aqueous hypochlorous acid. It is a colourless liquid, miscible with water, and boiling at 128°. By oxidation with chromic acid mixture it is converted into monochloracetic acid:

$$C_2H_4(OH)Cl + O_2 = H_2O + C_2H_3ClO_2.$$

By heating with potassium iodide it is converted into ethene iodhydrin, $C_2H_4(HO)I$, a viscid liquid, which decomposes when distilled.

Ethene Nitrate, $C_2H_4(NO_3)_2$, produced by heating ethene iodide with silver nitrate in alcoholic solution, or by dissolving glycol in a mixture of strong nitric and sulphuric acid, is a yellowish liquid, of specific gravity 1·483 at 8°, insoluble in water, exploding when heated. By alkalis is resolved into glycol and nitric acid.



Ethene-sulphuric Acid, $C_2H_4 . SO_4H_2 = SO_2{<}\begin{smallmatrix}OH\\OC_2H_5\end{smallmatrix}$, is produced by heating glycol with sulphuric acid. Its barium salt, obtained by neutralising the cooled acid solution with barium carbonate, is very soluble, deliquescent, and decomposes when heated with baryta-water into ethene and barium sulphate.

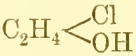
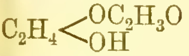
Ethene Oxide.—C_2H_4O, or $O{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}$, isomeric with acetic aldehyde is formed by the action of caustic potash on ethene chlorhydrin. The action is violent, and the ethene oxide is given off in vapour, which may be condensed in a receiver surrounded by a freezing mixture, and containing a few lumps of calcium chloride, over which the product may be afterwards dried. It is an ethereal mobile liquid, having a specific gravity of 0·898 at 0°, boiling at 13·5° (aldehyde boils at 21°), and miscible in all proportions with water and with alcohol. When the aqueous solution is treated with *sodium amalgam*, in a vessel surrounded with a freezing mixture, the ethene oxide takes up hydrogen, and is converted into ethyl alcohol:

$$C_2H_4O + H_2 = C_2H_6O.$$

Ethene oxide unites with *ammonia* in several proportions, forming the following basic compounds, all of which are syrupy liquids:

Monoxethenamine, ...	$C_2H_4O . NH_3$
Dioxethenamine, ...	$(C_2H_4O)_2 . NH_3$
Trioxethenamine, ...	$(C_2H_4O)_3 . NH_3$
Tetroxethenamine, ...	$(C_2H_4O)_4 . NH_3.$

This character distinguishes ethene oxide from aldehyde, which forms with ammonia a crystalline compound not possessing basic properties. A further distinction between these two isomeric bodies is, that aldehyde forms crystalline compounds with the acid sulphites of the alkali-metals, a property not possessed by ethene oxide.

Ethene oxide is a powerful base, uniting directly with *acids*, precipitating magnesia from a solution of magnesium chloride at ordinary temperatures, and ferric oxide and alumina from their saline solutions at 100°. With *hydrochloric acid*, it forms ethene chlorhydrin,  $C_2H_4{<}^{Cl}_{OH}$, and with *acetic acid*, ethene acetohydrin,  $C_2H_4{<}^{OC_2H_3O}_{OH}$. It also unites with *water* in several proportions, forming glycol and the following compounds.

Polyethenic Alcohols.—These are bodies which contain the elements of two or more molecules of ethene oxide combined with one molecule of water, and may be regarded as formed by the union of two or more molecules of glycol (mono-ethenic alcohol), with elimination of a number of water-molecules less by one than the number of glycol-molecules which enter into combination; or as derived from three or more molecules of water, by substitution of ethene for the whole of the hydrogen except two atoms; thus:

$C_2H_6O_2$ or $(C_2H_4)H_2O_2$ Monethenic alcohol (glycol).	=	$C_2H_4O.\ H_2O$ Ethene oxide.		
$C_4H_{10}O_3$ or $(C_2H_4)_2H_2O_3$ Diethenic alcohol.	=	$2C_2H_4O.H_2O$ Ethene oxide.	=	$2C_2H_6O_2 - H_2O$ Glycol.
$C_6H_{14}O_4$ or $(C_2H_4)_3H_2O_4$ Triethenic alcohol.	=	$3C_2H_4O.H_2O$ Ethene oxide.	=	$3C_2H_6O_2 - 2H_2O$ Glycol.
$C_8H_{18}O_5$ or $(C_2H_4)_4H_2O_5$ Tetrethenic alcohol.	=	$4C_2H_4O.H_2O$ Ethene oxide.	=	$4C_2H_6O_2 - 3H_2O$ Glycol.
$C_{2n}H_{4n+2}O_{n+1}$ or $(C_2H_4)_nH_2O_{n+1}$ *n*-ethenic alcohol.	=	$nC_2H_4O.H_2O$ Ethene oxide.	=	$nC_2H_6O_2 - (n-1)H_2O$ Glycol.

The polyethenic alcohols are formed—1. By heating ethene oxide with water in sealed tubes. In this manner Wurtz obtained diethenic alcohol together with monethenic, and a small quantity of tri-ethenic alcohol.—2. By heating ethene oxide with glycol in sealed tubes: this process yields the di- and tri-ethenic alcohols. 3. By heating glycol with ethene bromide in sealed tubes to 100°–120°. The first products of this reaction are diethenic alcohol, ethene bromhydrin and water:

$$\underset{\text{Monethenic alcohol.}}{3(C_2H_4)H_2O_2} + \underset{\text{Ethene bromide.}}{C_2H_4Br_2} = \underset{\text{Diethenic alcohol.}}{(C_2H_4)_2H_2O_3} + \underset{\text{Ethene bromhydrin.}}{2(C_2H_4)Br(OH)} + H_2O\,;$$

and the other polyethenic alcohols are formed, each from the one next below it in the series, by the action of ethene bromhydrin, according to the general equation:

$$(C_2H_4)_nH_2O_{n+1} + (C_2H_4)Br(OH) = (C_2H_4)_{n+1}H_2O_{n+2} + HBr\,.$$

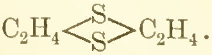
The hydrobromic acid thus formed then acts on the excess of glycol present, reproducing ethene bromhydrin, and thus the action is continued. By this process, the 2-, 3-, 4-, 5-, and 6-ethenic alcohols have been obtained and separated by fractional distillation; and when a sufficient excess of glycol is present, the temperature being kept between 110° and 120°, still higher members of the series are produced.

The polyethenic alcohols are syrupy liquids, becoming more viscid as their molecular weight increases: their boiling point rises by about 45° for each addition of C_2H_4O.

Diethenic alcohol, $C_4H_{10}O_3$ or $(C_2H_4)_2H_2O_3$, boils at about 245°; the density of its vapour is 3·78 (air = 1); by calculation it should be 3·67, so that it exhibits the normal condensation to two volumes. By contact with platinum black, or by treatment with nitric acid, it is oxidised to diglycollic acid, $C_4H_6O_5$, an acid isomeric with malic acid, and formed from diethenic alcohol by substitution of O for H_2, just as glycollic acid, $C_2H_4O_3$, is formed from monethenic alcohol, $C_2H_6O_2$. *Triethenic alcohol,* $C_6H_{14}O_4$, or $(C_2H_4)_3H_2O_4$, is oxidised in like manner to ethene-diglycollic acid, $C_6H_{12}O_5$.

Ethene Hydrosulphide or **Thiohydrate.**—*Ethenic* or *glycolic mercaptan,* $C_2H_4(SH)_2$, formed by the action of ethene bromide on an alcoholic solution of potassium hydrosulphide, is a colourless oil, of specific gravity 1·12, boiling at 146°, insoluble in water, soluble in alcohol and ether. With *lead acetate* it forms a yellow precipitate consisting of $C_2H_4S_2Pb$, and similar compounds with other metallic salts.

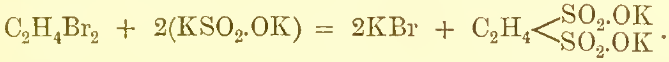
Ethene Sulphide, C_2H_4S, formed by the action of ethene bromide on potassium sulphide in alcoholic solution, is a crystalline body, melting at 110°, and boiling at 200°. Its vapour-density (H = 1) is 60, showing that its molecular formula is $(C_2H_4)_2S_2$. Its constitution is therefore



$C_2H_4\overset{S}{\underset{S}{<\!>}}C_2H_4$.

Ethene Hydroxysulphide or **Monothio-hydrate,** $C_2H_4(OH)(SH)$, formed by the action of ethene chlorhydrin on potassium hydrosulphide, is a liquid of similar properties, and forms salts in which half the hydrogen is replaced by a metal. Nitric acid oxidises it to isethionic acid, $C_2H_6SO_4$.

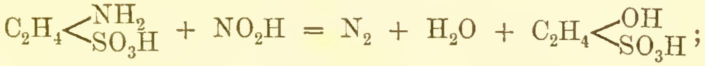
Ethene-sulphonic Acids.—*Ethene-disulphonic acid,* $C_2H_4<\substack{SO_3H\\SO_3H}$, is formed by oxidation of ethene hydrosulphide, $C_2H_4(SH)_2$, and ethene thiocyanate, $C_2H_4(CNS)_2$; by the action of fuming sulphuric acid on alcohol or ether; and by boiling ethene bromide with a strong solution of potassium sulphite:



$$C_2H_4Br_2 + 2(KSO_2.OK) = 2KBr + C_2H_4<\substack{SO_2.OK\\SO_2.OK}.$$

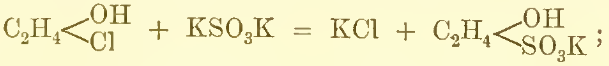
It forms a thick liquid, very soluble in water, difficult to crystallise; the crystallised acid melts at 94°. The barium salt, $C_2H_4(SO_3)_2Ba$, crystallises from water in six-sided tables.

Ethene-hydrinsulphonic acid, or *Isethionic acid,* $C_2H_4<\substack{OH\\SO_3H}$, isomeric with ethylsulphuric acid, $SO_2<\substack{OH\\OC_2H_5}$, is produced by the oxidation of ethene mono-thiohydrate, $C_2H_4<\substack{OH\\SH}$, with nitric acid; by the action of nitrous acid on taurine:



$$C_2H_4<\substack{NH_2\\SO_3H} + NO_2H = N_2 + H_2O + C_2H_4<\substack{OH\\SO_3H};$$

by heating ethene-chlorhydrin with potassium sulphite:

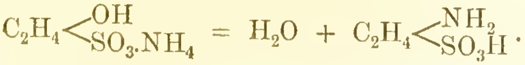


$$C_2H_4<\substack{OH\\Cl} + KSO_3K = KCl + C_2H_4<\substack{OH\\SO_3K};$$

and by boiling ethionic acid with water (p. 174).

When vapour of sulphuric anhydride is passed into well cooled alcohol or ether, and the product is boiled with water for several hours, a solution is formed, containing ethionic, sulphuric, and a small quantity of methionic acid; and on saturating this liquid with barium carbonate, filtering from barium sulphate, and leaving the filtrate to cool, methionate of barium crystallises out first, and afterwards the isethionate.

Isethionic acid is a viscid liquid, which does not easily crystallise: it is not decomposed by boiling with water. Its salts are stable, and crystallise well. The *ammonium salt* crystallises in rhombic plates melting at 190°; when heated to 210°–220°, it is converted into amidethylsulphonic acid or taurine:



$$C_2H_4<\substack{OH\\SO_3.NH_4} = H_2O + C_2H_4<\substack{NH_2\\SO_3H}.$$

By the action of phosphorus pentachloride on isethionic acid or its salts, the chloride, $C_2H_4Cl.SO_2Cl$, is formed, as a liquid which boils at 200°, and is converted by boiling with water into chlorethylsulphonic acid, $C_2H_4Cl.SO_3H$.

Taurine, $C_2H_4(NH_2).SO_3H$, occurs in combination with cholic acid (as taurocholic acid), in the bile of oxen and other animals, and in various other animal secretions. It may be prepared by boiling taurocholic acid with an alkali:

$$\underset{\text{Taurocholic acid.}}{C_{26}H_{45}NSO_7} + H_2O = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Taurine.}}{C_2H_7NSO_3}$$

It is formed artificially, as already observed, by heating ammonium isethionate to 230°; also by heating chlorethylsulphonic acid with aqueous ammonia.

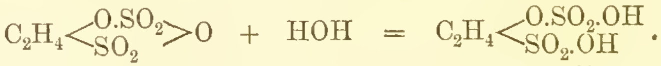
Taurine crystallises in large monoclinic prisms, easily soluble in hot water, insoluble in alcohol, melting and decomposing at about 240°. It forms salts with alkalis, and dissolves in acids, but separates from the solution unaltered.

Taurine is not decomposed by boiling with acids or with alkalis, but by fusion with potassium hydroxide it is decomposed in the manner shown by the equation:

$$C_2H_4(NH_2).SO_3K + 2KOH = C_2H_3KO_2 + SO_3K_2 + NH_3 + H_2.$$

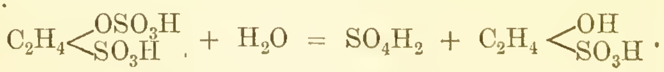
Nitrous acid converts it into isethionic acid.

Ethionic acid and *Anhydride.*—The anhydride, $C_2H_4S_2O_6$, formerly called *sulphate of carbyl*, is formed by passing the vapour of sulphur trioxide into anhydrous alcohol; also by direct union of ethene with sulphur trioxide. It is a very deliquescent crystalline mass, which melts at 80°. It readily takes up the elements of water, and is converted into ethionic acid, $C_2H_6S_2O_7$;



$$\underset{\text{Anhydride.}}{C_2H_4{<}\begin{matrix}O.SO_2\\SO_2\end{matrix}{>}O} + HOH = \underset{\text{Acid.}}{C_2H_4{<}\begin{matrix}O.SO_2.OH\\SO_2.OH\end{matrix}}.$$

Ethionic acid, having one of its sulphur-atoms connected with a carbon-atom directly, the other only through the medium of oxygen, acts both as a sulphonic acid and as an acid ether of sulphuric acid; it is therefore bibasic. Both the free acid and its salts are resolved by boiling with water into sulphuric and isethionic acids:



$$C_2H_4{<}\begin{matrix}OSO_3H\\SO_3H\end{matrix} + H_2O = SO_4H_2 + C_2H_4{<}\begin{matrix}OH\\SO_3H\end{matrix}.$$

ETHIDENE COMPOUNDS.

Ethidene dichloride, $CH_3—CHCl_2$, has already been described (p. 70). The *oxide*, $CH_3—CHO$, is ordinary aldehyde (see ALDEHYDES).

Ethidene Dimethylate, $CH_3—CH(OCH_3)_2$, occurs in crude wood-spirit, and is formed in the oxidation of a mixture of methylic and ethylic alcohols; also by heating aldehyde with methyl alcohol. It is a colourless, ethereal liquid, having a specific gravity of 0·8555, and boiling at 65°.

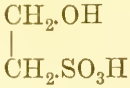
Ethidene Methyl-ethylate, $CH_3—CH\Big<\begin{matrix}OCH_3\\OC_2H_5\end{matrix}$, formed simultaneously with the preceding by the oxidation of a mixture of methyl and ethyl alcohol, boils at 85°.

Ethidene Diethylate or *Acetal*, $CH_3—CH(OC_2H_5)_2$, isomeric with ethene diethylate, is formed by oxidation of ethyl alcohol, and is found among the first portions of the distillate obtained in the preparation of ordinary spirit. It is formed also by the action of sodium ethylate on ethidene dichloride, and by heating aldehyde with alcohol to 100° in sealed tubes :

$$CH_3—CHO + 2(C_2H_5OH) = H_2O + CH_3—CH(OC_2H_5)_2.$$

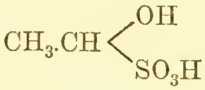
It is a liquid smelling like alcohol, having a specific gravity of 0·821 at 22°, boiling at 104°. With *chlorine* it yields mono-, di-, and trichloracetal.

Ethidene-sulphonic acids.—The relation of these somewhat unstable acids to their isomerides, the ethene-sulphonic acids, is shown by the following formulæ :



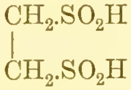
$$\begin{matrix}CH_2.OH\\|\\CH_2.SO_3H\end{matrix}$$

Isethionic acid.



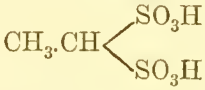
$$CH_3.CH\Big<\begin{matrix}OH\\SO_3H\end{matrix}$$

Ethidene-oxysulphonic acid.



$$\begin{matrix}CH_2.SO_2H\\|\\CH_2.SO_2H\end{matrix}$$

Ethene-disulphonic acid.

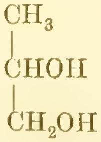


$$CH_3.CH\Big<\begin{matrix}SO_3H\\SO_3H\end{matrix}$$

Ethidene-disulphonic acid.

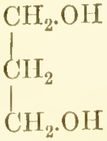
Ethidene-disulphonic acid, $CH_3.CH(SO_3H)_2$, and *Ethidene-chlorosulphonic acid*, $CH_3.CH\Big<\begin{matrix}Cl\\SO_3H\end{matrix}$, are formed by heating ethidene dichloride (p. 70) with an aqueous solution of neutral sodium sulphite to about 140°. The former is very unstable; the latter is moderately stable, and forms well crystallised salts : its sodium salt crystallises in nacreous laminæ.

Propene Glycols, $C_3H_8O_2 = C_3H_6(OH)_2$.—There are two of these diatomic alcohols, represented by the following formulæ:



$$\begin{matrix}CH_3\\|\\CHOH\\|\\CH_2OH\end{matrix}$$

Propene glycol.



$$\begin{matrix}CH_2.OH\\|\\CH_2\\|\\CH_2.OH\end{matrix}$$

Trimethene glycol.

They are analogous to the second and fourth modifications of the diatomic haloïd derivatives of propene, already described (p. 70). Glycols analogous to the first and third of these derivatives, viz., $CH_3—CH_2—CX_2$ and $CH_3—CX_2—CH_3$ are not known, and probably cannot exist, since it appears, as already noticed, that two hydroxyl groups cannot be attached to one carbon-atom.

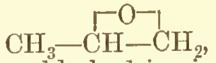
Propene glycol is formed by heating the corresponding bromide, $CH_3—CHBr—CH_2Br$, with silver acetate, and the resulting acetic ether with potash; also by heating propene chloride with water and lead oxide. It is a colourless oily liquid, having a sweet taste, a specific gravity of 1·051 at 0°, and boiling at 188°–189°. In contact with platinum black it is oxidised to lactic acid:

$$CH_3—CHOH—CH_2OH + O_2 = H_2O + CH_3—CHOH—COOH.$$

Heated to 100° with strong hydriodic acid, it gives pseudopropyl iodide, $CH_3—CHI—CH_3$. Phosphorus pentachloride converts it into propene dichloride, $CH_3—CHCl—CH_2Cl$.

Propene chlorhydrin, $CH_3—CHOH—CH_2Cl$, is formed by the action of gaseous hydrogen chloride on the glycol, and by that of hypochlorous acid on propene. It has a specific gravity of 1·302 at 0°, and boils at 127°.

The corresponding *bromhydrin* boils at about 146°.



Propene oxide, $CH_3—\overset{\ulcorner\!-O-\!\urcorner}{CH—CH_2}$, formed by the action of aqueous potash on propene chlorhydrin, is a volatile liquid, boiling at 35°, having a specific gravity of 0·859 at 0°, easily soluble in water. Nascent hydrogen converts it into secondary propyl alcohol, $CH_3—CHOH—CH_3$.

Trimethene glycol, prepared from trimethene bromide (p. 72), is a thick saccharine liquid, boiling at 212°.

Butene Glycols, $C_4H_{10}O_2 = C_4H_8(OH)_2$.—Six of these compounds are theoretically possible, four derived from normal butane and two from isobutane. Only two of them, however, are at present known, viz.:

(1.) *Butene glycol*, $CH_3—CHOH—CH_2—CH_2OH$, is formed in small quantity by the action of sodium amalgam on acetic aldehyde in aqueous solution; but is best prepared by leaving a cold mixture of acetic aldehyde and dilute hydrochloric acid to itself for two or three days, whereby the acetic aldehyde is converted into the aldehyde of butene glycol, called aldol, and treating the latter with sodium amalgam:

$$\underset{\text{Acetic aldehyde (2 mol.).}}{CH_3—CHO + CH_3—CHO} = \underset{\text{Aldol.}}{CH_3—CHOH—CH_2—CHO}$$

and

$$\underset{\text{Aldol.}}{CH_3—CHOH—CH_2—CHO} + H_2 = \underset{\text{Butene glycol.}}{CH_3—CHOH—CH_2—CH_2OH.}$$

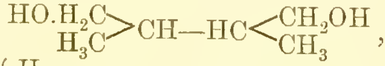
Butene glycol is a thick liquid, boiling at 204°, miscible with water and with alcohol. By oxidation with nitric acid or with chromic acid mixture it is resolved into acetic and oxalic acids, together with a small quantity of butyric aldehyde.

(2.) *Isobutene glycol*, $(CH_3)_2{=}COH{-}CH_2OH$, prepared from the corresponding bromide, has a specific gravity of 1·048 at 0°, and boils at 183°–184°. By oxidation with nitric acid it is converted into oxyisobutyric acid, $(CH_3)_2{=}COH{-}COOH$.

Isopentene or **Amylene Glycol**, $C_5H_{10}(OH)_2 = (CH_3)_2{=}CH{-}CHOH{-}CH_2OH$, the only 5-carbon glycol known, is prepared by distilling amylene diacetate with potash, or by addition of hydrogen dioxide to amylene. It boils at 177°, has a specific gravity of 0·987 at 0°, and is converted by oxidation with nitric acid into isovaleric acid. The corresponding oxide, $C_5H_{10}O$, is a liquid insoluble in water, having a specific gravity of 0·824 at 0°, and boiling at 95°.

Hexene Glycols, $C_6H_{12}(OH)_2$.—*Normal hexene glycol*, $CH_2OH{-}(CH_2)_4{-}CH_2OH$, from hexene bromide (obtained from mannite, or from the hexyl chloride of American petroleum), has a specific gravity of 0·967 at 0°, and boils at 207°.

Mesohexene Glycol,



$\begin{matrix}HO.H_2C\\H_3C\end{matrix}{>}CH{-}HC{<}\begin{matrix}CH_2OH\\CH_3\end{matrix}$, or *Diallyl Dihydrate*, $C_6H_{10}\left\{\begin{matrix}H_2\\(OH)_2\end{matrix}\right.$, is prepared by heating diallyl in a sealed flask with strong hydriodic acid, converting the resulting diallyl hydriodide, $C_6H_{10}\left\{\begin{matrix}H_2\\I_2\end{matrix}\right.$, into the diacetate, $C_6H_{10}\left\{\begin{matrix}H_2\\(OC_2H_3O)_2\end{matrix}\right.$, by treating it with silver acetate suspended in ether, and decomposing the diacetate with potash. It is a thick, colourless syrup, having a specific gravity of 0·9638 at 0° and 0·9202 at 65°; boils between 212° and 215°.

Pinacone, $(CH_3)_2COH{-}COH(CH_3)_2$, is formed, together with pseudopropyl alcohol, by the action of sodium or sodium-amalgam on acetone in aqueous solution:

$$(CH_3)_2CO + CO(CH_3)_2 + H_2 = (CH_3)_2COH{-}COH(CH_3)_2.$$

It crystallises from the concentrated aqueous solution as a hydrate, $C_6H_{14}O_2+6H_2O$, in large square tables which melt at 42°, and gradually effloresce in contact with the air. The hydrate gives up its water when heated, and at 171°–172° yields a distillate of anhydrous pinacone, which solidifies to an indistinctly crystalline mass, melting at 38°, and reconverted into the hydrate by solution in water. Pinacone, when heated with acids, is converted into pinacolin, $C_6H_{12}O$ (see ALDEHYDES.)

TRIATOMIC ALCOHOLS AND ETHERS.

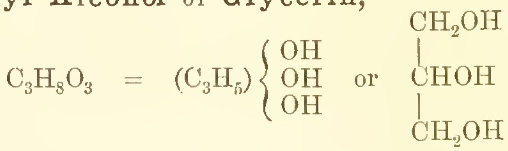
Triatomic alcohols may be derived from saturated hydrocarbons by substitution of three atoms of hydroxyl for three atoms of hydrogen, and may accordingly be regarded as compounds of trivalent alcohol-radicles with three atoms of hydroxyl, or as compounds derived from a triple molecule of water, H_6O_3, by substitution of a trivalent alcohol-radicle for three atoms of hydrogen. The hydrocarbons of the series C_nH_{2n+2}, should accordingly yield a series of triatomic alcohols of the form $(C_nH_{2n-1})(OH)_3$, viz.:—

Methenyl alcohol, . . .	$CH(OH)_3$
Ethenyl alcohol, ...	$C_2H_3(OH)_3$
Propenyl alcohol, . . .	$C_3H_5(OH)_3$
Tetrenyl alcohol, . . .	$C_4H_7(OH)_3$
Pentenyl alcohol, . . .	$C_5H_9(OH)_3$
&c.	&c.

Of these, however, only two are known, viz., propenyl alcohol, or glycerin, and pentenyl alcohol, or amyl glycerin.

Each triatomic alcohol subjected to the action of acids, or of the chlorides, bromides, or iodides of phosphorus, may yield three classes of ethers, derived from it by substitution of a halogen element, or acid radicle, for part or the whole of the hydroxyl; thus, from glycerin may be obtained the three hydrochloric ethers, $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2OH$, $C_3H_5Cl_3$, and the three acetic ethers, $C_3H_5(OC_2H_3O)(OH)_2$, $C_3H_5(OC_2H_3O)_2OH$, and $C_3H_5(OC_2H_3O)_3$.

Propenyl Alcohol or **Glycerin,**



$$C_3H_8O_3 \quad = \quad (C_3H_5)\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right. \quad \text{or} \quad \begin{array}{l}CH_2OH\\ \mid\\ CHOH\\ \mid\\ CH_2OH\end{array}$$

This compound is obtained by the action of alkalis on natural fats, which are, in fact, the propenylic ethers of certain fatty acids; thus stearin, one of the constituents of mutton suet, consists of *propenyl tristearate*, $(C_3H_5)(OC_{18}H_{35}O)_3$, a compound derivable from glycerin itself, by substitution of stearyl, $C_{18}H_{35}O$, for hydrogen. Now, when stearin is boiled with a caustic alkali, it is converted into a stearate of the alkali-metal and glycerin; thus:

$$\underset{\text{Stearin.}}{C_3H_5(OC_{18}H_{35}O)_3} + 3KHO = \underset{\substack{\text{Potassium}\\ \text{stearate.}}}{3KOC_{18}H_{35}O} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}$$

A similar reaction takes place when any other similarly constituted fat is treated with a caustic alkali. The metallic salts of the fatty acids thus obtained are the well known bodies called soaps, and the process is called saponification; this term, originally restricted to actual soap-making, has been extended to all cases of the resolution of a compound ether into an acid and an alcohol, such, for example, as the conversion of ethyl acetate into acetic acid and ethyl alcohol by the action of alcoholic potash.

Glycerin was originally obtained by heating together olive or other suitable oil, lead oxide, and water, as in the manufacture of common *lead-plaster;* an insoluble soap of lead is thereby formed, while the glycerin remains in the aqueous liquid. The latter is treated with sulphuretted hydrogen, digested with animal charcoal, filtered, and evaporated in a vacuum at the temperature of the air. Glycerin is now produced in very large quantity and perfect purity in the decomposition of fatty substances by means of over-heated steam, a process which Mr. George Wilson has introduced into the manufacture of candles. In this reaction a fatty acid and glycerin are produced by assimilation of the elements of water; they are carried over by the excess of steam in a state of mechanical mixture, which rapidly separates into two layers in the receiver. The reaction is exactly similar to that which takes place when a caustic alkali is used to effect the saponification, *e.g.*:

$$\underset{\text{Stearin.}}{C_3H_5(OC_{18}H_{35}O)_3} + 3H_2O = \underset{\text{Stearic acid.}}{3HOC_{18}H_{35}O} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}$$

Glycerin may also be produced from propenyl bromide, $(C_3H_5)Br_3$, a compound formed, as already observed, by the action of bromine on allyl iodide, C_3H_5I. The process consists in converting the propenyl bromide into propenyl triacetate, $(C_3H_5)(OC_2H_3O)_3$, by the action of silver acetate, and decomposing this ether with potash. This mode of formation must not, however, be regarded as an actual synthesis of glycerin from compounds of simpler constitution: for the allyl-compounds are themselves prepared from glycerin (p. 162).

Glycerin is a nearly colourless and very viscid liquid of specific gravity 1·27, and boiling at 290°. When quite pure and anhydrous, it crystallises on exposure to a very low temperature especially if agitated, as in railway transport. The crystals are monoclinic, perfectly colourless, and melt at 60° F.* Glycerin has an intensely sweet taste, and mixes with water in all proportions: its solution does not undergo the alcoholic fermentation, but when mixed with yeast and kept in a warm place, it is gradually converted into propionic acid. Glycerin has no action on vegetable colours. Exposed to heat, it volatilises in part, darkens, and decomposes, giving off, amongst other products, a substance called *acrolein*, C_3H_4O, having an intensely pungent odour.

Concentrated *nitric acid* converts glycerin into glyceric acid, $C_3H_6O_4$, an acid related to glycerin in the same manner as glycollic acid to glycol, and acetic acid to ethyl alcohol; being formed from it by substitution of oxygen for two atoms of hydrogen in immediate relation to hydroxyl; thus:

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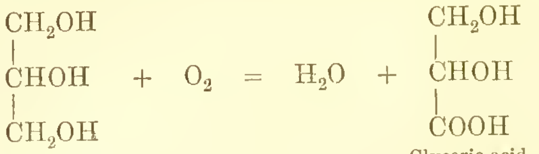
* Roos, Chem. Soc. J. 1876, i. 651.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + O_2 = H_2O + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Glycerin. Glyceric acid.

The formula of glycerin indicates the possibility of effecting a second substitution of the same kind, which would yield diglyceric acid, $C_3H_4O_5$, but this acid has not been actually obtained.

Glycerin, treated with a mixture of strong nitric and sulphuric acids, forms nitroglycerin, $C_3H_5(NO_2)_3O_3$, a heavy oily liquid which explodes powerfully by percussion. It is much used for blasting in mines and quarries, but is very dangerous to handle, and has given rise to several fatal accidents.

Glycerin combines with the elements of sulphuric acid, forming a sulphoglyceric acid, $C_3H_8O_3SO_3$, which gives soluble salts with lime, baryta, and lead oxide.

Monatomic *oxygen-acids* (acetic, benzoic, stearic, &c.), heated in sealed tubes with glycerin, yield compound ethers in which 1, 2, or 3 hydrogen-atoms of the glycerin are replaced by an equivalent quantity of the acid radicle, according to the proportions employed. The resulting compound ethers are denoted by names ending in *in*; thus:

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{HOC_2H_3O} = \underset{\text{Mono-acetin.}}{C_3H_5(OH)_2OC_2H_3O} + H_2O$$

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{2HOC_2H_3O} = \underset{\text{Diacetin.}}{C_3H_5(OH)(OC_2H_3O)_2} + 2H_2O$$

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{3HOC_2H_3O} = \underset{\text{Triacetin.}}{C_3H_5(OC_2H_3O)_3} + 3H_2O\,.$$

The glyceric ethers or glycerides thus produced are, for the most part, oily liquids, increasing in viscidity as the acid from which they are formed has a higher mocular weight; those formed from the higher members of the fatty acid series, $C_nH_{2n}O_2$ (such as palmitic and stearic acids), are solid fats. Some of the triacid glycerides, produced artificially in the way just mentioned, are identical with natural fats occurring in the bodies of plants and animals; thus tristearin is identical with the stearin of beef and mutton suet: triolein with the olein of olive oil, &c.

Hydrochloric and *hydrobromic acids* act upon glycerin in the same manner as oxygen-acids, excepting that the reaction always stops at the second stage (just as in the action of these acids on the glycols it stops at the first stage). The ethers thus formed are called chlohydrins, bromhydrins, &c., *e.g.:*

$$\begin{array}{ccccccc} C_3H_5(OH)_3 & + & HCl & = & C_3H_5(OH)_2Cl & + & H_2O \\ \text{Glycerin.} & & & & \text{Chlorhydrin.} & & \end{array}$$

$$\begin{array}{ccccccc} C_3H_5(OH)_3 & + & 2HCl & = & C_3H_5(OH)Cl_2 & + & 2H_2O \\ \text{Glycerin.} & & & & \text{Dichlorhydrin.} & & \end{array}$$

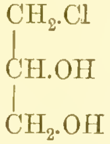
Hydriodic acid acts somewhat differently, producing an ether, $C_6H_{11}IO_3$, which may be regarded as a double molecule of glycerin, having four equivalents of hydroxyl replaced by two atoms of oxygen, and a fifth by iodine, $C_6H_{10}O_2(OH)I$.

The *chlorides* and *bromides of phosphorus* act upon glycerin in the same manner as hydrochloric and hydrobromic acid, but their action goes on to the third stage, producing trichlorhydrin, or propenyl chloride, and the corresponding bromine-compound:

$$\begin{array}{ccccccccc} C_3H_5(OH)Cl_2 & + & PCl_5 & = & PCl_3O & + & HCl & + & C_3H_5Cl_3 \\ \text{Dichlorhydrin.} & & & & & & & & \text{Trichlorhydrin.} \end{array}$$

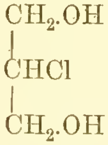
Iodide of phosphorus acts on glycerin in a totally different manner, yielding iodopropene or allyl iodide, C_3H_5I (p. 163).

Monochlorhydrins, $C_3H_5\left\{\begin{matrix}(OH)_2\\ Cl\end{matrix}\right.$.—Of these compounds there are two modifications, viz.:



$$\begin{array}{l} CH_2.Cl \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

Unsymmetrical.



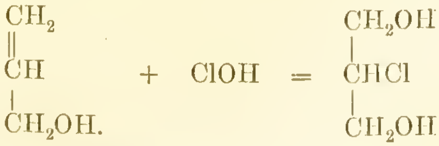
$$\begin{array}{l} CH_2.OH \\ | \\ CHCl \\ | \\ CH_2.OH \end{array}$$

Symmetrical.

The first is the chief product obtained by saturating glycerin with hydrochloric acid gas, and heating the liquid for some time over the water-bath. To purify it, the acid liquid is saturated with sodium carbonate, then agitated with ether, the ethereal solution is evaporated, and the residual liquid subjected to fractional distillation.

Unsymmetrical chlorhydrin is a viscid liquid, easily soluble in water, alcohol, and ether, having a specific gravity of 1·31, and boiling at 220°–227°; converted by sodium amalgam into ordinary propene-glycol, $CH_3—CH(OH)—CH_2OH$.

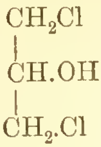
Symmetrical chlorhydrin is obtained by agitating allyl alcohol with aqueous hypochlorous acid:

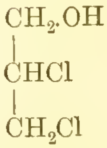


$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH. \end{array} + ClOH = \begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}$$

It has a specific gravity of 1·4 at 13°, and boils at 230°–235°.

Dichlorhydrins, $C_3H_5\left\{\begin{matrix}OH\\Cl_2\end{matrix}\right.$. — Of these also there are two modifications, viz.:

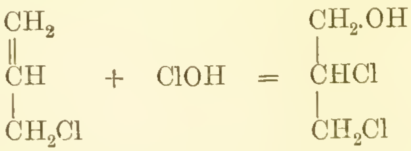

$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH \\ | \\ CH_2.Cl \end{array}$$
Symmetrical.


$$\begin{array}{l} CH_2.OH \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}$$
Unsymmetrical.

Both are formed by heating glycerin with strong hydrochloric acid, the first, however, predominating. This, which is the ordinary modification, is best prepared by saturating a mixture of equal volumes of glycerin and glacial acetic acid with hydrochloric acid gas at 100°, neutralising the product with sodium carbonate, and subjecting it to fractional distillation. It may also be prepared by distilling glycerin with S_2Cl_2. Lastly, it may be obtained quite pure by mixing epichlorhydrin, C_3H_5OCl, with fuming hydrochloric acid.

Symmetrical dichlorhydrin, or *dichlorinated pseudopropyl alcohol,* is a liquid having an ethereal odour, a specific gravity of 1·383 at 19°, boiling at 174°, easily soluble in alcohol and ether, sparingly in water. By *sodium amalgam* it is converted into pseudopropyl alcohol, $CH_3{-}CHOH{-}CH_3$, and by *oxidation* with dilute chromic acid mixture, into acetone dichloride, $CH_3{-}Cl_2{-}CH_3$. With *potassium cyanide* it forms dicyanhydrin, $CH_2.CN{-}CH(OH){-}CH_2.CN$.

Unsymmetrical Dichlorhydrin (commonly called *chloride of allyl alcohol*) is formed by addition of chlorine to allyl alcohol, $CH_2{=}CH{-}CH_2(OH)$, or of hypochlorous acid to allyl chloride:


$$\begin{array}{lcccl} CH_2 & & & & CH_2.OH \\ \| & & & & | \\ CH & + & ClOH & = & CHCl \\ | & & & & | \\ CH_2Cl & & & & CH_2Cl \end{array}$$

It has a specific gravity of 1·379 at 0°; boils at 182°–183°; is converted by metallic sodium into allyl alcohol.

By the action of caustic potash or soda, both dichlorhydrins are converted, by abstraction of HCl, into epichlorhydrin.

Trichlorhydrin, *Glyceryl trichloride,* or *Allyl trichloride,* $C_3H_5Cl_3 = CH_2Cl{-}CHCl{-}CH_2Cl$, is formed by the action of phosphorus pentachloride on either of the dichlorhydrins; also (together with $CH_3.CHCl.CHCl_2$) by the action of iodine chloride on propene chloride, $CH_3.CHCl.CH_2Cl$; and by chlorination of propene and of pseudopropyl iodide. It is a liquid which smells like chloroform, has a specific gravity of 1·417 at 15°, and boils at 158°. Heated with solid potassium or sodium hydroxide, it forms dichloroglycide, $CH_3{=}CCl{-}CH_2Cl$, boiling at 94°. Heated with sulphuric acid, it forms monochloracetone, $CH_3{-}CO{-}CH_2Cl$.

Bromhydrins.—*Monobromhydrin*, $C_3H_5(OH)_2Br = CH_2.Br{-}CH.OH{-}CH_2.OH$, obtained by the action of hydrobromic acid on glycerin, is an oily liquid, boiling in a vacuum at 180°.

Symmetrical Dibromhydrin, $CH_2Br{-}CH.OH{-}CH_2Br$, prepared from glycerin and hydrobromic acid, is a liquid having an ethereal odour, a specific gravity of 2·11 at 18°, and boiling at 219°. *Unsymmetrical dibromhydrin*, $CH_2Br{-}CHBr{-}CH_2OH$, from allyl alcohol and bromine, boils at 212–214°.

Tribromhydrin, *Glyceryl tribromide*, or *Allyl tribromide*, $C_3H_5Br_3 = CH_2Br{-}CHBr{-}CH_2Br$, is obtained by the action of bromine on allyl iodide:

$$C_3H_5I + 2Br_2 = IBr + C_3H_5Br_3.$$

It crystallises in colourless, shining prisms, melts at 16°, boils at 219°–220°; is converted by caustic potash or soda into dibromoglycide, $CH_2{=}CBr{-}CH_2Br$, boiling at 151°–152°.

Iodhydrins.—*Monoiodhydrin*, $C_3H_5\left\{\begin{matrix}(OH)_2\\ I\end{matrix}\right.$, obtained by heating glycerin to 100° with hydriodic acid, is a viscid liquid, having a specific gravity of 1·783.

Di-iodhydrin, $C_3H_5(OH)I_2 = CH_2I.CH(OH).CH_2I$, obtained by heating symmetrical dichlorhydrin with aqueous potassium iodide, is a thick oil, having a specific gravity of 2·4, and solidifying to a crystalline mass at $-15°$.

Tri-iodhydrin or *Glyceryl tri-iodide*, $C_3H_5I_3$, does not appear to be capable of existing, inasmuch as the action of hydriodic acid, or of iodine and phosphorus on glycerin yields nothing but allyl iodide and free iodine.

Glycide compounds.—When dichlorhydrin is treated with potash, it gives up a molecule of hydrochloric acid, and is converted into a compound, C_3H_5OCl, called epichlorhydrin:

$$C_3H_5(OH)Cl_2 - HCl = C_3H_5OCl.$$

This compound may be regarded as the hydrochloric ether of an alcohol, $C_3H_5O(OH)$, called *glycide*, formed from glycerin by abstraction of H_2O. Dibromhydrin, $C_3H_5(OH)Br_2$, treated in the same manner, yields epibromhydrin, or the hydrobromic ether of glycide, C_3H_5OBr. Epichlorhydrin heated with dry potassium iodide is converted into epi-iodhydrin, C_3H_5OI:

$$C_3H_5OCl + KI = KCl + C_3H_5OI.$$

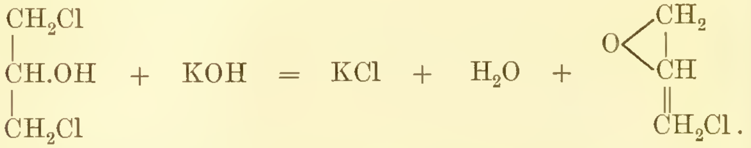
These glycidic ethers are easily reconverted into bodies of the glycerin type. Thus epichlorhydrin combines with acetic acid, forming glyceric acetochlorhydrin:

$$(C_3H_5)ClO + HOC_2H_3O = (C_3H_5)Cl(OH)(OC_2H_3O);$$

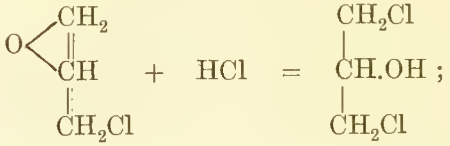
and with alcohol in like manner, forming glyceric ethylchlorhydrin, $(C_3H_5)Cl(OH)(OC_2H_5)$.

Epichlorhydrin unites directly with *water*, forming glyceric monochlorhydrin, $C_3H_5(OH)_2Cl$.

Epichlorhydrin or *Glycidic Hydrochloride*, isomeric with monochloracetone, may be obtained by agitating either of the dichlorhydrins with strong potash-ley:



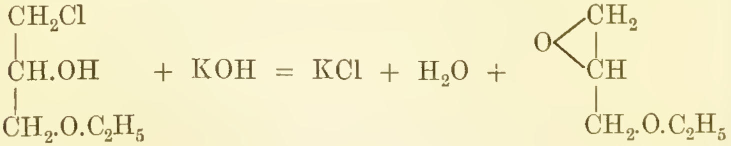
It is a mobile liquid, having a specific gravity of 1·194 at 0°, boiling at 119°; insoluble in water; easily soluble in alcohol and ether. It smells like chloroform, and has a burning sweetish taste. When heated with fuming *hydrochloric acid*, it is converted into symmetrical dichlorhydrin:



and by prolonged heating with water, into monochlorhydrin. Heated with *alcohols*, it yields ethers of chlorhydrin, such as

$$C_3H_5\left\{\begin{matrix}Cl\\OH\\O.C_2H_5\end{matrix}\right.$$

, which, when distilled with potassium hydroxide, are converted into alcoholic glycides or glycidic ethers; thus:



Ethylic chlorhydrin. Ethyl glycide.

Ethyl-glycide, $C_3H_5.O.OC_2H_5$ (or epiethylin), boils at 126°–130°; *amyl-glycide*, $C_3H_5.O.O.C_5H_{11}$, at 188°.

Epibromhydrin, C_3H_5OBr, from either of the two bromhydrins, boils at 139°–140°; *epi-iodhydrin*, C_3H_5OI, obtained by heating epichlorhydrin with solution of potassium iodide, boils at about 160°.

Trichlorhydrin, heated with potassium hydroxide, which abstracts HCl, yields dichloroglycide, $C_3H_4Cl_2 = CH_2{=}CCl{-}CH_2Cl$.

Alcoholic Ethers of Glycerin.—Derivatives of glycerin containing alcohol-radicles are formed by heating the mono- and dichlorhydrins with sodium-alcohol, thus:

$$\underset{\text{Dichlorhydrin.}}{C_3H_5\left\{\begin{matrix}OH\\Cl_2\end{matrix}\right.} + 2(C_2H_5.O.Na) = 2NaCl + \underset{\text{Diethylin.}}{C_3H_5\left\{\begin{matrix}OH\\(O.C_2H_5)_2\end{matrix}\right.}.$$

Mono-ethylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\OC_2H_5\end{matrix}\right.$, is soluble in water, and boils at 230°. Diethylin is sparingly soluble in water, smells like peppermint, has a specific gravity of 0·92, and boils at 191°. Triethylin, $C_3H_5(O.C_2H_5)_3$, formed by the action of ethyl iodide on the sodium-derivative of diethylin, is a liquid insoluble in water, boiling at 185°.

Allylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O.C_3H_5\end{matrix}\right.$, is produced by heating glycerin with oxalic acid, and occurs (together with glyceric oxide) in the residue left after heating the product to 260°. It is a viscid liquid, boiling at 225°–240°.

Glyceric oxide or glycerin-ether, $(C_3H_5)_2O_3$, occurring together with allylin, as just mentioned, boils at 169°–172°.

The ethers of glycerin containing acid radicles, including the natural oils and fats, will be described under the respective acids.

Polyglycerins.—Two, three, or more molecules of glycerin can unite into a single molecule, with elimination of a number of water-molecules less by one than the number of glycerin molecules which combine together; thus:

$$\underset{\text{Glycerin.}}{2C_3H_5(OH)_3} - H_2O = \underset{\text{Diglycerin.}}{(C_3H_5)_2\left\{\begin{matrix}O\\(OH)_4\end{matrix}\right.}$$

$$\underset{\text{Glycerin.}}{3C_3H_5(OH)_3} - 2H_2O = \underset{\text{Triglycerin.}}{(C_3H_5)_3\left\{\begin{matrix}O_2\\(OH)_5\end{matrix}\right.}$$

Generally:

$$nC_3H_5(OH)_3 - (n-1)H_2O = (C_3H_5)_n\left\{\begin{matrix}O_{n-1}\\(OH)_{n+2}\end{matrix}\right..$$

The product is a polyglycerin whose atomicity (determined by the number of equivalents of hydroxyl contained in it) is $n+2$.

The mode of preparing the polyglycerins is similar to that of the polyethenic alcohols (p. 171), and consists in heating glycerin with monochlorhydrin, whereby diglycerin and hydrochloric acid are formed:

$$C_3H_5Cl(OH)_2 + C_3H_5(OH)_3 = (C_3H_5)_2O(OH)_4 + HCl.$$

The hydrochloric acid thus formed converts a fresh quantity of glycerin into chlorhydrin, which then acts in a similar manner on the diglycerin, and converts it into triglygerin; and in this manner the process is continued. The polyglycerins may then be separated by fractional distillation. Their properties are but little known.

Isopentenyl Alcohol, or **Amyl Glycerin,** $C_5H_{12}O_3 = (C_5H_9)(OH)_3$.—This compound is formed from bromoisopentene dibromide, $C_5H_9Br.Br_2$, or isopentenyl bromide, $C_5H_9Br_3$, by the series of processes represented in the following equations:

$$\begin{array}{ccccccc} C_5H_9Br & + & 2AgOC_2H_3O & = & 2AgBr & + & C_5H_9\left\{\begin{matrix}(OC_2H_3O)_2\\ Br\end{matrix}\right. \\ \text{Isopentenyl bromide.} & & \text{Silver acetate.} & & \text{Silver bromide.} & & \text{Isopentenyl diacetobromhydrin.} \end{array}$$

$$\begin{array}{ccccccc} C_5H_9\left\{\begin{matrix}(OC_2H_3O)_2\\ Br\end{matrix}\right. & + & 2KOH & = & 2KOC_2H_3O & + & C_5H_9\left\{\begin{matrix}(OH)_2\\ Br\end{matrix}\right. \\ \text{Isopentenyl diacetobromhydrin.} & & \text{Potassium hydrate.} & & \text{Potassium acetate.} & & \text{Isopentenyl bromhydrin.} \end{array}$$

$$\begin{array}{ccccccc} C_5H_9\left\{\begin{matrix}(OH)_2\\ Br\end{matrix}\right. & + & KOH & = & KBr & + & (C_5H_9)(OH)_3 \\ \text{Isopentenyl bromhydrin.} & & & & & & \text{Isopentenyl alcohol.} \end{array}$$

Amyl glycerin is a thick colourless liquid, having a sweet aromatic taste, and soluble in water.

TETRATOMIC ALCOHOLS AND ETHERS.

The only tetratomic alcohol at present known is:

Erythrite, $C_4H_{10}O_4 = (C_4H_6)(OH)_4$, also called *Erythromannite, Erythroglucin,* and *Phycite,* which is the tetratomic alcohol analogous to butyl alcohol, $C_4H_{10}O$, and butene glycol, $C_4H_{10}O_2$; the corresponding glycerin is not known.

Erythrite is a saccharine substance, existing ready-formed in *Protococcus vulgaris.* It was originally discovered by Dr. Stenhouse among the products of decomposition of erythric acid.* It crystallises in large transparent prisms, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether: not fermentable. Heated with *hydriodic acid,* it yields secondary butyl iodide. C_4H_0I (p. 146):

$$C_4H_{10}O_4 + 7HI = C_4H_9I + 4H_2O + 3I_2.$$

Heated with *oxygen-acids,* it forms compound ethers, in the manner of alcohols in general; thus, with *benzoic acid,* $C_7H_6O_2$, or HOC_7H_5O, it forms a dibenzoate, $(C_4H_6)(OH)_2(OC_7H_5O)_2$, and a hexbenzoate, $(C_4H_6)(OC_7H_5O)_4.2C_7H_2O_2$, consisting of neutral benzoyl-erythrite united with two molecules of benzoic acid.

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* See the Chapter on Colouring Matters.

A tetratomic ether, viz., Ethylic Orthocarbonate or Orthocarbonic Ether, $C(OC_2H_5)_4$, analogous to carbon tetrachloride, CCl_4, is formed by the action of sodium ethylate on chloropicrin (p. 80):

$$CCl_3(NO_2) + 4NaOC_2H_5 = 3NaCl + NaNO_2 + C(OC_2H_5)_4 .$$

It is a liquid having an ethereal odour, and boiling at 158°–159°. Heated with ammonia, it yields guanidine, CN_3H_5, and ethyl alcohol:

$$C(OC_2H_5)_4 + 3NH_3 = CN_3H_5 + 4C_2H_5OH .$$

The corresponding alcohol, $C(OH)_4$, has probably no existence, inasmuch as one carbon-atom appears to be incapable of linking together two or more hydroxyl groups.

HEXATOMIC ALCOHOLS AND ETHERS.

This class of compounds includes most of the saccharine substances found in plants, and others produced from them by artificial transformation. Three of the natural sugars, mannite, dulcite, and sorbite, having the composition $C_6H_{14}O_6$, or $C_6H_8(OH)_6$, are saturated hexatomic alcohols derived from the saturated hydrocarbon, C_6H_{14}. Several others, called glucoses, contain $C_6H_{12}O_6$, that is to say, two atoms of hydrogen less than mannite and dulcite, and may therefore be regarded—so far as composition is concerned—as the aldehydes of these alcohols; moreover, ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen, just as acetic aldehyde, C_2H_4O, is converted into common alcohol, C_2H_6O. Further, there are diglucosic alcohols, or saccharoses, $C_{12}H_{22}O_{11}(=2C_6H_{12}O_6 - H_2O)$, related to glucoses in the same manner as diethenic alcohol to glycol, or diglycerin to glycerin: the most important of these are cane-sugar and milk-sugar; and, lastly, there are certain vegetable products called amyloses—viz., starch, cellulose, and a few others, represented by the formula $C_6H_{10}O_5$, or multiples thereof, which may be regarded as the oxygen-ethers or anhydrides of the glucoses, or of the diglucosic alcohols, inasmuch as they differ therefrom by a molecule of water.

These three groups of compounds, which consist of carbon united with hydrogen and oxygen in the proportion to form water, are included under the general name of carbohydrates.

Saturated Hexatomic Alcohols.

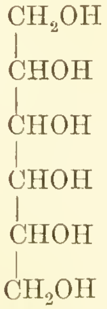
Mannite, $C_6H_{14}O_6 = (C_6H_8)(OH)_6$.—This is the chief component of *manna*, an exudation from a species of ash; it is also found in the juice of certain other plants, in several sea-weeds, and in mushrooms. It is best prepared by treating manna with boiling alcohol, and filtering the solution whilst hot; it then crystallises on cooling in tufts of slender needles. Mannite may be produced artificially by treating a solution of glucose with sodium-amalgam, the glucose then taking up 2 atoms of hydrogen:

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

The same transformation of glucose sometimes takes place under the action of certain ferments.

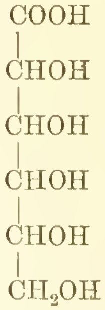
Mannite crystallises in thin four-sided prisms, easily soluble in water and in hot alcohol, insoluble in ether. It is slightly sweet, melts at 166°, has no action on polarised light, and is not fermentable, except under very unusual conditions.

By oxidation in contact with *platinum black*, mannite is converted into mannitic acid, $C_6H_{12}O_7$, and mannitose, $C_6H_{12}O_6$, a kind of sugar isomeric with glucose. By oxidation with *nitric acid* it yields saccharic acid, $C_6H_{10}O_8$, and ultimately oxalic acid. Mannitic acid and saccharic acid are related to mannite in the same manner as glycollic acid and oxalic acid to glycol; the relation between the three compounds is shown by the following formulæ:



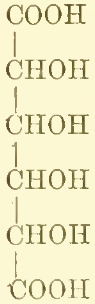
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Mannite.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Mannitic acid.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Saccharic acid.

By *fuming nitric acid*, or more easily by a mixture of *nitric* and *sulphuric acids*, mannite is converted into nitromannite, $C_6H_8(NO_2)_6O_6$, a crystalline body which explodes violently by percussion or when suddenly heated, and is reconverted into mannite by ammonium sulphide. With sulphuric acid mannite forms sulphomannitic acid, $C_6H_{14}O_6.3SO_3$.

Mannite, treated with *hydriodic acid*, is converted into secondary hexyl iodide, or hexene hydriodide (p. 154):

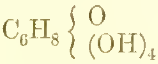
$$C_6H_{14}O_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2.$$

Mannite, heated with *organic acids*, forms compound ethers, after the manner of alcohols in general, the elements of the mannite and the acid uniting together, with elimination of one or more molecules of water. The resulting compounds, called mannitanides, bear a considerable resemblance to the fats; but their composition has not been very exactly determined.

These ethers, when saponified with alkalis, yield, not mannite, but mannitan, $C_6H_{12}O_5$, a compound differing from mannite by one molecule of water. The same compound is obtained in small quantity by heating mannite to 200°, and more easily by prolonged boiling of mannite with strong hydrochloric acid. It is a syrupy liquid, which volatilises slowly at 140°, and dissolves easily in water and in cold absolute alcohol: this last property affords the means of separating it from mannite. When exposed to the air, it slowly absorbs water, and is reconverted into mannite; the change is accelerated by boiling with acids or with alkalis.

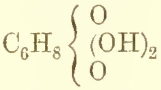
Mannite, boiled with *butyric acid*, gives up two molecules of water, and is converted into mannide, $C_6H_{10}O_4$, which is also a syrupy liquid, but differs from mannitan in being much more volatile, evaporating rapidly at 140°, and in being quickly reconverted into mannite by exposure to moist air. It dissolves easily in water, and in absolute alcohol.

The two anhydrides of mannite may be represented by the following formulæ:



$$C_6H_8\left\{\begin{array}{l}O\\(OH)_4\end{array}\right.$$

Mannitan.



$$C_6H_8\left\{\begin{array}{l}O\\(OH)_2\\O\end{array}\right.$$

Mannide.

Dulcite, $C_6H_{14}O_6$, also called *Dulcin*, *Dulcose*, and *Melampyrite*. —This sugar, isomeric with mannite, is obtained from a crystalline substance of unknown origin, imported from Madagascar: it is extracted therefrom by boiling with water, and crystallises from the filtered solution. Dulcite is likewise obtained from *Melampyrum nemorosum*, by mixing the aqueous decoction of the plant with lime, concentrating, adding hydrochloric acid in slight excess, and evaporating a little: it then separates in crystals as the liquid cools.

Dulcite is a sweet substance resembling mannite in most of its properties, but differing from it in its crystalline form, which is that of a monoclinic prism, whereas the crystals of mannite are trimetric; also in its melting point, dulcite melting at 182°, mannite at 166°, and by yielding, when oxidised with nitric acid, not saccharic acid, but mucic acid, which is isomeric therewith. Dulcite, heated with hydriodic acid, yields a secondary hexyl alcohol, identical with that obtained from mannite. Heated with organic acids, it forms ethers called dulcitanides, analogous to the mannitanides, and yielding by saponification, not dulcite, but dulcitan, $C_6H_{12}O_5$, which may likewise be obtained by heating dulcite, or by boiling it with hydrochloric acid. *Hexacetodulcite*, $C_6H_8(OC_2H_3O)_6$, melts at 171°.

Isodulcite, $C_6H_{14}O_6$, or $C_6H_{12}O_5.H_2O$, a saccharine substance isomeric with mannite and dulcite, is produced by the action of dilute acids on quercitrin, a yellow substance occurring in quercitron bark. It forms large transparent, regularly developed crystals resembling those of cane-sugar: it is sweeter than grape-sugar, not fermentable, dissolves in 2·09 parts of water at 18°, and easily in absolute alcohol. The solutions turn the plane of polarisation to the right. Isodulcite melts, with loss of water, between 105° and 110°, is coloured yellow or brown by strong sulphuric acid and caustic alkalis, and reduces cupric oxide. By a mixture of nitric and sulphuric acids, it is converted into a slightly explosive nitro-compound, $C_6H_9(NO_2)_3O_6$.

Sorbite, $C_6H_{14}O_6 + 1\frac{1}{2}H_2O$, occurs in the berries of the mountain-ash in small crystals, easily soluble in water. It gives off its water when heated, and melts at 110.

Mannite, dulcite, and sorbite are distinguished from the true sugars (glucoses and saccharoses) by not fermenting in contact with yeast, and by not reducing an alkaline solution of cupric oxide.

Pinite and **Quercite** are naturally occurring saccharine bodies, isomeric with mannitan and dulcitan.

Pinite is contained in the sap of a Californian pine (*Pinus Lambertiana*), and is deposited from the aqueons extract of the hardened juice, in hard white crystalline nodules, as sweet as cane-sugar, very soluble in water, nearly insoluble in alcohol. It turns the plane of polarisation of a luminous ray to the right; it is not fermentable. With *benzoic acid* it forms dibenzopinite, $C_6H_8\left\{\begin{array}{l}(OC_7H_5O)_2\\ O\\ (OH)_2\end{array}\right.$, and tetrabenzopinite, $C_6H_8\left\{\begin{array}{l}O\\ (OC_7H_5O)_4\end{array}\right.$; and similar compounds with *stearic acid*.

Quercite is a saccharine substance extracted from acorns, by treating the aqueous infusion with milk of lime to remove tannic acid, leaving the liquid to ferment with yeast to remove fermentable sugar, evaporating the filtrate to a syrup, and leaving it to crystallise. It forms hard monoclinic crystals, which grate between the teeth, and are soluble in water and in hot dilute alcohol. Heated in a sealed tube with *benzoic acid*, it forms dibenzoquercite, having the same composition as dibenzopinite.

CARBOHYDRATES.

This name, as already observed, is given to a class of compounds containing 6 or 12 atoms of carbon united with hydrogen and oxygen in the proportion to form water. They may be regarded as derivatives of the hexatomic alcohol, $C_6H_{14}O_6$, and are divided into the three following groups:

Glucoses,
$C_6H_{12}O_6$.
+ Grape-sugar[*]
or Dextrose.
− Fruit-sugar
or Levulose.
Mannitose.
+ Galactose.
Inosite.
Sorbin.
+ Eucalyn.
Dambose.

Saccharoses,
$C_{12}H_{22}O_{11}$.
+ Cane-sugar
or Saccharose.
+ Parasaccharose.
+ Melitose.
+ Melezitose.
+ Trehalose.
+ Mycose.
Synanthrose.
+ Milk-sugar
or Lactose.
+ Maltose.

Amyloses,
$C_6H_{10}O_5$.
+ Starch.
+ Dextrin.
+ Glycogen.
− Inulin.
Cellulose.
Tunicin.
Gum.

Most of these compounds occur in the vegetable organism; a few also, as dextrose, lactose, glycogen, and inosite, in the animal organism.

Glucoses, $C_6H_{12}O_6$.

The sugars included in this formula may be regarded as aldehydes of the saturated alcohols, $C_6H_{14}O_6$. Ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen (p. 188), and, on the other hand, mannite, when slowly oxidised in contact with platinum black, is partly converted into mannitose. Nevertheless, the glucoses still exhibit the characteristic property of alcohols, namely, that of forming ethers by combination with acids and elimination of water. The formula of a glucose may indeed be derived from that of mannite given on page 188, by removing two hydrogen-atoms from one of the groups, CH_2OH, the other groups remaining as before; the glucoses may therefore be expected to act as pentatomic alcohols. Bodies thus constituted may be called *alcoholic aldehydes*.

The following varieties of glucose are known:—

1. *Ordinary glucose*, produced by hydration of starch under the influence of dilute acids or of diastase, and existing ready-formed, together with other kinds of sugar, in honey and various fruits, especially in grapes, and alone in diabetic urine.
2. *Levulose*, existing in cane-sugar which has been acted upon by acids, and obtained pure by the action of dilute acids upon a variety of starch called inulin.
3. *Mannitose*, produced by oxidation of mannite.
4. *Galactose*, formed by the action of acids on milk-sugar.
5. *Inosite*, existing in muscular flesh.
6. *Sorbin*, obtained from mountain-ash berries.
7. *Eucalyn*, existing, together with another kind of sugar, in the so-called Australian manna.

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[*] The + sign indicates that the substance turns the plane of polarisation to the right; the − sign indicates rotation to the left.

8. *Dambose*, obtained from a saccharine substance existing in African caoutchouc.

The first three of these glucoses exhibit but very slight diversity in their chemical properties, differing chiefly indeed in their action on polarised light, and a few other physical properties. They all yield saccharic acid by oxidation. Galactose differs from them in yielding mucic acid when oxidised. Inosite, sorbin, and eucalyn exhibit still greater differences in their chemical properties, especially in not being fermentable, except under very peculiar circumstances, whereas the four other glucoses undergo vinous fermentation when placed, under certain conditions, in contact with yeast.

All the glucoses, except inosite, are decomposed by boiling with aqueous alkalis; this property distinguishes them from mannite and dulcite. They are not carbonised by strong sulphuric acid at ordinary temperatures. When boiled with a solution of potassio-cupric tartrate, they throw down the copper in the form of red cuprous oxide.

1. **Ordinary Glucose, Dextro-glucose, Dextrose,** $C_6H_{12}O_6$.—This variety of sugar is very abundantly diffused through the vegetable kingdom: it may be extracted in large quantity from the juice of sweet grapes (whence it is often called *grape-sugar*), also from honey, of which it forms the solid crystalline portion, by washing with cold alcohol, which dissolves the fluid syrup. The appearance of this substance, to an enormous extent, in the urine, is the most characteristic feature of the disease called *diabetes*. It exists in diabetic urine unmixed with any other kind of sugar, and is easily obtained by concentrating the liquid till it crystallises, washing the crystals with cold alcohol, dissolving them in water, and re-crystallising. It may also be prepared from starch by the action of diastase, a peculiar ferment existing in germinating barley, or by boiling with dilute sulphuric acid. In these reactions the starch takes up the elements of water, and is resolved into glucose and dextrin, a compound isomeric with starch itself.

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Dextrin.}}{2C_6H_{10}O_5}$$

Glucose, when required in considerable quantity, is always prepared from starch. Cellulose is likewise converted into glucose by the action of acids. Lastly, glucose is produced by boiling natural glucosides with dilute acids.

Glucose is much less sweet than cane-sugar, and less soluble in water and in alcohol; anhydrous glucose dissolves in 1·224 parts of water at 15°. From its aqueous solution it separates in granular warty masses, consisting of a hydrate, $C_6H_{12}O_6.H_2O$, which leaves anhydrous glucose as a fused transparent mass when heated to 100°, or as a dry white powder when heated to 55° or 60° in a stream of dry air. The alcoholic solution deposits anhydrous glucose in microscopic needles which melt at 140°. In the state of solution glucose turns the plane of polarisation of a ray of light to the right (hence the names *dextroglucose* and *dextrose*): its specific or molecular rotatory power is +56°, and does not vary with the temperature (pp. 37, 38).

Glucose may be heated to 120° or even 130° without alteration, but at 170° it gives off water, and is converted into glucosan, $C_6H_{10}O_5$, which, when freed from caramel (p. 198) by means of charcoal, and from glucose by fermentation, forms a colourless mass, scarcely sweet to the taste, and having somewhat less dextro-rotatory power than glucose. At higher temperatures glucose blackens and suffers complete decomposition. Glucose boiled for some time with *dilute sulphuric* or *hydrochloric acid*, is converted into brown substances called ulmin, ulmic acid, &c.—*Strong sulphuric acid* converts it at ordinary temperatures into sulpho-saccharic acid, $C_6H_{12}O_5SO_3$, which forms a soluble barium salt.

Lime, *baryta*, and *lead oxide* dissolve slowly in aqueous solution of glucose, and on adding alcohol to the liquid, compounds of these oxides with glucose are precipitated. The barium compound is said to contain $(C_6H_{12}O_6)_2(BaO)_3.2H_2O$; the calcium compound, $(C_6H_{12}O_6)_2(CaO)_3.2H_2O$; the lead compound, $(C_6H_{12}O_6)_2(PbO)_3(OH)_6$. These compounds are, however, very unstable, being decomposed at the heat of boiling water. Glucose also combines with *sodium chloride*, forming the compound $(C_6H_{12}O_6)_2NaCl.H_2O$.

Glucose, boiled with a *cupric salt* in presence of *alkalis*, easily reduces the cupric oxide to cuprous oxide: by this character it is easily distinguished from cane-sugar.

When solutions of cane-sugar and glucose are mixed with two separate portions of solution of cupric sulphate, and caustic potash is added in excess to each, deep-blue liquids are obtained, which, on being heated, exhibit different characters: the one containing cane-sugar is at first but little altered; a small quantity of red powder falls after a time, but the liquid long retains its blue tint; with the glucose, on the other hand, the first application of heat throws down a copious greenish precipitate, which rapidly changes to scarlet, and eventually to dark-red cuprous oxide, leaving a nearly colourless solution. If only small quantities of material are available, a mixture of cupric sulphate and tartaric acid, to which an excess of potash has been added, may be used with advantage. This solution, called *potassio-cupric tartrate*, is an excellent test for distinguishing the two varieties of sugar, or discovering an admixture of glucose with cane-sugar.

Glucose mixed in dilute solution with *yeast* and exposed to a temperature of 21°–26°, easily undergoes vinous fermentation (p. 129).

2. **Levulose**, $C_6H_{12}O_6$.—This sugar, distinguished from dextrose by turning the plane of polarisation to the left, occurs, together with dextrose, in honey, in many fruits, and in other saccharine

substances. The mixture of these two sugars in equivalent quantities constitutes fruit-sugar, or invert sugar, which is itself levorotatory, because the specific rotatory power of levulose is, at ordinary temperatures, greater than that of dextrose.

Cane-sugar may be *inverted*, that is, transformed into a mixture of equal parts of dextrose and levulose, by warming with dilute acids:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

The same change is brought about by contact with yeast, or with pectase, the peculiar ferment of fruits; it likewise takes place slowly when a solution of cane-sugar is left to itself.

To separate the levulose, the invert sugar obtained from 10 grams of cane-sugar is mixed with 6 grams of slaked lime and 100 grams of water, whereby a solid calcium-compound of levulose is formed, while the whole of the dextrose remains in solution, and may be separated from the precipitate by pressure. The calcium salt of levulose, suspended in water and decomposed by carbon dioxide, yields a solution of pure levulose, which may be filtered and concentrated by evaporation. Levulose may be at once obtained in the pure state by the action of dilute acids on inulin.

Levulose is a colourless uncrystallisable syrup, as sweet as cane-sugar, more soluble in alcohol than dextrose. Its rotatory power is much greater than that of dextrose at ordinary temperatures, but diminishes as the temperature rises. For the transition tint between the blue and the purple, $[\alpha] = -106°$ at 14°; $= -79{\cdot}5°$ at 52°; $= -53°$ at 90°. Now, the rotatory power of dextrose is the same at all temperatures, and equal to $+56°$; consequently that of invert sugar, which is $-25°$ at 15°, diminishes by about one-half at 52°, becomes nothing at 90°, and changes sign above that temperature.

Levulose exhibits, for the most part, the same chemical reactions as dextrose, but is more easily altered by heat or by acids, and on the contrary offers greater resistance to the action of alkalis or of ferments.

Levulosan, $C_6H_{10}O_5$, the oxygen-ether or anhydride of levulose, is produced, together with dextrose, by melting cane-sugar for some time at 160°:

$$C_{12}H_{22}O_{11} = C_6H_{10}O_5 + C_6H_{12}O_6.$$

The dextrose may be removed from the liquid by fermentation, and the levulosan, which is unfermentable, may be obtained by evaporation as an uncrystallisable syrup. By boiling with water or dilute acids, it is converted into a fermentable levorotatory sugar, probably levulose.

3. **Mannitose**, $C_6H_{12}O_6$.—This is the sugar produced, together with mannitic acid, by the oxidation of mannite in contact with platinum black. It may be separated by saturating the liquid with

lime, precipitating the calcium mannitate with alcohol, evaporating the filtrate to a syrup, adding alcohol, again filtering, and evaporating to dryness.

Mannitose is syrupy, uncrystallisable, fermentable, inactive to polarised light, and resembles the other glucoses in its chemical reaction.

4. **Galactose**, $C_6H_{12}O_6$, is produced by boiling milk-sugar with dilute acids. It is soluble in water, sparingly soluble in cold alcohol, crystallises more readily than ordinary glucose; has a dextrorotatory power of 83·3°; and is very easily fermentable. It resembles dextrose in most of its reactions, but is distinguished from all the four glucoses above described by yielding mucic instead of saccharic acid, when oxidised by nitric acid.

5. **Inosite**, or **Phaseomannite**, $C_6H_{12}O_6$, is a variety of glucose occurring in the muscular substance of the heart and other organs of the animal body; also in green kidney beans, the unripe fruit of *Phaseolus vulgaris*, and in many other plants. It forms prismatic crystals, resembling gypsum, soluble in water, but insoluble in alcohol and ether. It may be boiled with a strong aqueous potash or baryta without alteration or coloration. If this sugar be evaporated with nitric acid nearly to dryness, the residue mixed with a little ammonia and calcium chloride, and again evaporated, a beautiful and characteristic rose tint is produced.

Inosite does not ferment with yeast, but in contact with cheese, flesh, or decaying membrane and chalk, it undergoes lactous fermentation, producing lactic, butyric, and carbonic acids.

6. **Sorbin**, $C_6H_{12}O_6$, is a crystallisable sugar existing in the juice of ripe mountain-ash berries (*Sorbus aucuparia*). The juice, when allowed to stand for some time in open vessels, deposits a brown crystalline matter, which may be obtained in transparent colourless crystals belonging to the trimetric system. This substance is almost insoluble in alcohol, but easily soluble in water, to which it imparts an exceedingly sweet taste. A solution of sorbin, mixed with ammonia and lead acetate, yields a white flocculent precipitate, containing $C_{12}H_{18}Pb_3O_{12}.PbO_6$. With *sodium chloride* it forms a compound which crystallises in cubes.

Sorbin is converted by *nitric acid* into tartaric, racemic, and aposorbic acids. It does not ferment with yeast, but in contact with cheese and chalk, at 40°, it undergoes lactous fermentation, yielding a large quantity of lactic acid, together with alcohol and butyric acid.

7. **Eucalyn**, $C_6H_{12}O_6$, is an unfermentable sugar, separated in the fermentation of melitose (the sugar of the *Eucalyptus* of Tasmania), in consequence of the destruction of a fermentable kind of sugar, which, in combination with eucalyn, constitutes melitose:

$$\underset{\text{Melitose.}}{C_{12}H_{22}O_{11}} + H_2O = 2CO_2 + \underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Eucalyn.}}{C_6H_{12}O_6}$$

On evaporating the liquid, the eucalyn remains as an uncrystallisable syrup, having a specific rotatory power of + 165° nearly. It is not rendered fermentable by the action of sulphuric acid.

8. **Dambose,** $C_6H_{12}O_6$, obtained by heating dambonite with hydriodic acid, crystallises in six-sided prisms, melting at 212°.

Dambonite, its methylic ether, $C_6H_{10}(CH_3)_2O_6$, occurs in a peculiar kind of caoutchouc from the Gaboon in West Africa, from which it may be extracted by alcohol. It crystallises from alcohol in six-sided prisms, dissolves easily in water, melts at 190°, and sublimes at 200°–210° in slender shining needles.

GLUCOSIDES.—When ordinary glucose is heated to 100°–120° for fifty or sixty hours with acetic, butyric, stearic, benzoic, and other organic acids, the two unite, with elimination of water, and compound ethers called glucosides are formed, analogous to the mannitanides. A number of these artificial glucosides have been prepared by Berthelot, who regards them as derivatives of *glucosan*, $C_6H_{10}O_5$, because when heated with alkalis they yield glucosan, not glucose. Thus, there is a glucoso-butyric ether to which Berthelot assigns the formula $C_6H_8(C_4H_7O)_2O_5$, and an acetic ether, which he regards as hexaceto-glucosan, $C_6H_4(C_2H_3O)_6O_5$; but they are merely oily liquids, which are very difficult to obtain pure, and therefore their analyses are not much to be depended on.

A considerable number of bodies of similar constitution exist ready formed in plants, many of them constituting the bitter principles of the vegetable kingdom. None of these natural glucosides have been produced artificially, but they are all resolved by boiling with dilute acids into glucose and some other compound. The most important of them will be described in a future chapter.

POLYGLUCOSIC ALCOHOLS.

The compounds of this group, including cane-sugar and other bodies more or less resembling it, may be regarded as formed by the combination of two or more molecules of glucose, with elimination of a number of molecules of water, less by one than the number of glucose molecules which enter in the combination:

$$2C_6H_{12}O_6 - H_2O = C_{12}H_{22}O_{11}, \text{ Diglucosic alcohol.}$$
$$3C_6H_{12}O_6 - 2H_2O = C_{18}H_{32}O_{16}, \text{ Triglucosic alcohol.}$$
$$nC_6H_{12}O_6 - (n-1)H_2O = C_{6n}H_{10n+2}O_{5n+1}.$$

The only known alcohols of this class are diglucosic alcohols, $C_{12}H_{22}O_{11}$; but starch, cellulose, and other plant-constituents, appear to be the oxygen-ethers, or anhydrides, of polyglucosic alcohols of higher orders.

Cane-sugar or **Saccharose,** $C_{12}H_{22}O_{11}$.—This most useful substance is found in the juice of many of the grasses, in the sap of several forest trees, in the root of the beet and the mallow, and in several other plants. Most sweet fruits contain cane-sugar, together with invert sugar (p. 194); some, as walnuts, hazel-nuts, almonds, coffee-beans, and St. John's-bread (the fruit of *Ceratonia siliqua*), contain only cane-sugar. Honey and the nectars of flowers contain cane-sugar together with invert sugar; the sugar in the nectary of cactuses is almost wholly cane-sugar.

Sugar is extracted most easily and in greatest abundance from the sugar-cane (*Saccharum officinarum*), cultivated for the purpose in many tropical countries. The canes are crushed between rollers, and the expressed juice is suffered to flow into a large vessel, where it is slowly heated nearly to its boiling point. A small quantity of slaked lime mixed with water is then added, which occasions the separation of a coagulum consisting chiefly of earthy phosphates, waxy matter, a peculiar albuminous principle, and mechanical impurities. The clear liquid separated from the coagulum is rapidly evaporated in open pans, heated by a strong fire made with the crushed canes of the preceding year, which have been dried in the sun, and preserved for the purpose. When sufficiently concentrated, the syrup is transferred to a shallow vessel, and left to crystallise, during which time it is frequently agitated in order to hasten the change and hinder the formation of large crystals. It is lastly drained from the dark uncrystallisable syrup, or *molasses*, and sent into commerce, under the name of *raw* or *Muscovado* sugar. The refining of this crude product is effected by redissolving it in water, adding a quantity of albumin in the shape of serum of blood or white of egg, and sometimes a little lime-water, and heating the whole to the boiling point: the albumin coagulates, and forms a kind of network of fibres, which enclose and separate from the liquid all mechanically suspended impurities. The solution is decolorised by filtration through animal charcoal, evaporated to the crystallising point, and put into conical earthen moulds, where it solidifies, after some time, to a confusedly crystalline mass, which is drained, washed with a little clean syrup, and dried in a stove: the product is ordinary *loaf-sugar*. When the crystallisation is allowed to take place quietly and slowly, *sugar-candy* results, the crystals under these circumstances acquiring large volume and regular form. The evaporation of the decolorised syrup is best conducted in strong close boilers exhausted of air: the boiling point of the syrup is reduced in consequence from 110° C. (230° F.) to 65·5° C. (150° F.), or below, and the injurious action of the heat upon the sugar is in great measure prevented. Indeed, the production of molasses in the rude colonial manufacture is chiefly the result of the high and long-continued heat applied to the cane-juice, and might be almost entirely prevented by the use of vacuum-pans, the product of sugar being thereby greatly increased in quantity, and so far improved in quality as to become almost equal to the refined article.

In many parts of the continent of Europe, sugar is manufactured on a large scale from beet-root, which contains about 8 per cent. of that substance. The process is far more complicated and troublesome than that just described, and the raw product much inferior. When refined, however, it is scarcely to be distinguished from the preceding. In the Western States of America sugar is prepared in considerable quantity from the sap of the sugar maple (*Acer saccharinum*), which is common in those parts. The tree is tapped in the spring by boring a hole a little way into the wood, and inserting a small spout to convey the liquid into a vessel placed for its reception. This is boiled down in an iron pot, and furnishes a coarse sugar, which is almost wholly employed for domestic purposes, but little finding its way into commerce.

Pure sugar slowly separates from a strong solution in large, transparent, colourless crystals, having the figure of a modified monoclinic prism. The crystals have a specific gravity of 1·6, and are unchangeable in the air. Sugar has a pure, sweet taste, is very soluble in water, requiring for solution only one-third of its weight in the cold, and is also dissolved by alcohol, but less easily. When moderately heated it melts, and solidifies on cooling to a glassy amorphous mass, familiar as *barley-sugar.*

Cane-sugar, heated a little above 160°, is converted, without loss of weight, into a mixture of dextrose and levolusan (p. 194):

$$C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5 .$$

At a higher temperature, water is given off, the dextrose being probably converted into glucosan (p. 193): afterwards, at about 210°, more water goes off, and a brown substance called caramel remains, consisting of a mixture of several compounds, all formed from sugar by elimination of water. At a still higher temperature, an inflammable gaseous mixture is given off, consisting of carbon monoxide, marsh gas, and carbon dioxide; a distillate is obtained, consisting of brown oils, acetic acid, acetone, and aldehyde; and a considerable quantity of charcoal remains behind. The brown oils contain a small quantity of furfurol, and a bitter substance called assamar.

By prolonged boiling with *water*, cane-sugar is converted into invert sugar. This transformation is accelerated by the presence of acids, and apparently also of certain salts. Different acids act with various degrees of rapidity—mineral more quickly than organic acids, sulphuric acid most quickly of all. By prolonged boiling even with very dilute acids, sugar is decomposed, yielding a number of brown amphorous products called ulmin, ulmic acid,* &c.;

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* Under the names *ulmin* and *ulmic acid* have been confounded a number of brown or black uncrystallisable substances produced by the action of powerful chemical agents upon sugar, lignin, &c., or generated by the putrefactive decay of vegetable fibre. Common garden mould, for example, treated with dilute, boiling solution of caustic potash, yields a deep-brown solution, from which acids precipitate a flocculent, brown substance, having but a slight degree of solubility in water. This is generally called *ulmic* or *humic* acid, and its origin is ascribed to the reaction of the alkali on the *ulmin* or *humus* of the soil. These bodies differ exceedingly in composition, and are too indefinite to admit of ready investigation.

if the air has access to the liquid, formic acid is likewise produced. Concentrated hydrochloric acid decomposes sugar very quickly.

Strong sulphuric acid decomposes dry sugar when heated, and a concentrated solution, even at ordinary temperatures, with copious evolution of sulphurous oxide, and formation of a large quantity of black carbonaceous matter. By this reaction cane-sugar may be distinguished from glucose.

Cane-sugar is very easily oxidised. It reduces silver and mercury salts when heated with them, and precipitates gold from the chloride. Pure cupric hydrate is but slowly reduced by it, even at the boiling heat ; in presence of alkali, however, a blue solution is formed, and on boiling the liquid, cuprous oxide is slowly precipitated (p. 193). Cane-sugar takes fire when triturated with 8 parts of lead dioxide, and forms with potassium chlorate a mixture which detonates on percussion, and burns vividly when a drop of oil of vitriol is let fall upon it. Distilled with a mixture of sulphuric acid and manganese dioxide, it yields formic acid. Heated with dilute nitric acid, it yields saccharic and oxalic acids. 1 part sugar mixed with 3 parts nitric acid, of specific gravity 1·25 to 1·30, and heated to 50°, is wholly converted into saccharic acid:

$$C_{12}H_{22}O_{11} + O_6 = 2C_6H_{10}O_8 + H_2O .$$

At the boiling heat, the product consists chiefly of oxalic acid. Very strong nitric acid, or a mixture of strong nitric and sulphuric acids, converts sugar into nitrosaccharose, probably $C_{12}H_{18}(NO_2)_4O_{11}$. Sugar is likewise oxidised by chloride of lime, but the products have not been examined.

Cane-sugar does not turn brown when triturated with alkalis, a character by which it is distinguished from glucose : it combines with them, however, forming compounds called sucrates. By boiling with potash-ley it is decomposed, but much more slowly than the glucoses.

Potassium- and *Sodium-compounds* of cane-sugar, $C_{12}H_{21}KO_{11}$ and $C_{12}H_{21}NaO_{11}$, are formed, as gelatinous precipitates, on mixing an alcoholic solution of cane-sugar with potash or soda-ley.

A *barium-compound*, $C_{12}H_{20}BaO_{11} . H_2O$, or $C_{12}H_{22}O_{11} . BaO$, is obtained, as a crystalline precipitate, on adding hydrate or sulphide of barium to an aqueous solution of sugar. It may be crystallised from boiling water, but is insoluble in alcohol.

Calcium compounds.—Lime dissolves in sugar-water much more rapidly than in pure water. The solution has a bitter taste, and is completely but slowly precipitated by carbonic acid. There are three or four of these compounds, which may be approximately represented by the following formulæ:

1. $C_{12}H_{22}O_{11} . CaO$. 3. $C_{12}H_{22}O_{11} . 2CaO . 2H_2O$.
2. $2C_{12}H_{22}O_{11} . 3CaO$ (?) 4. $C_{12}H_{22}O_{11} . 3CaO$.

Magnesia and *lead oxide* are also dissolved by sugar-water. A crystalline lead-compound, $C_{12}H_{18}Pb_2O_{11}$, is precipitated on mixing sugar-water with neutral lead-acetate and ammonia.

Sugar also form crystalline compounds with *sodium chloride.*

Cane-sugar is not directly fermentable, but when its dilute aqueous solution is mixed with yeast, and exposed to a warm atmosphere, it is first resolved into a mixture of dextrose and levulose, which then enter into fermentation, yielding alcohol and carbon dioxide.

Parasaccharose, $C_{12}H_{22}O_{11}$.—This is an isomeride of cane-sugar, produced, according to Jodin,* by spontaneous fermentation. An aqueous solution of cane-sugar containing ammonium phosphate, left to itself for three months in summer, yielded, under circumstances not further specified, a crystalline sugar, isomeric with saccharose, together with an amorphous sugar having the composition of a glucose, both dextro-rotatory. Parasaccharose is very soluble in water, nearly insoluble in alcohol of 90 per cent. Its specific rotatory power at 10° = +108°, appearing to increase a little with rise of temperature. It does not melt at 100°, but becomes coloured, and appears to decompose. It reduces an alkaline cupric solution, but only half as strongly as dextro-glucose. It is not perceptibly altered by dilute sulphuric acid, even at 100°; hydrochloric acid weakens its rotatory power, turns the solution brown, and heightens its reducing power for cupric oxide.

Melitose, $C_{12}H_{22}O_{11}$.—A kind of sugar obtained from the manna which falls in opaque drops from various species of *Eucalyptus* growing in Tasmania. It is extracted by water, and crystallises in extremely thin interlaced needles, having a slightly saccharine taste.

The crystals of melitose are hydrated, containing $C_{12}H_{22}O_{11}.3H_2O$. They give off 2 molecules of water at 100°, and become anhydrous at 130°. They dissolve in 9 parts of cold water, very easily in boiling water, and dissolve also in boiling alcohol more freely than mannite. The alcoholic solution yields small but well-developed crystals. The aqueous solution turns the plane of polarisation to the right: for the transition tint $[\alpha] = +102°$.

Melitose, heated with dilute sulphuric acid, is resolved into a fermentable sugar (probably dextrose), and non-fermentable eucalyn (p. 195). Melitose ferments in contact with yeast, but is resolved, in the first instance, into glucose and eucalyn. It does not reduce an alkaline cupric solution, and is not altered by boiling with dilute alkalis or with baryta-water. It is oxidised by nitric acid, yielding a certain quantity of mucic acid, together with a large quantity of oxalic acid.

Melezitose, $C_{12}H_{22}O_{11}$.—This variety of sugar is found in the so-called manna of Briançon, which exudes from the young shoots of the larch (*Larix europæa*). The manna is exhausted with alcohol, which, when evaporated, yields melezitose in very small, hard, shining, efflorescent crystals, which give off 4 per cent. of water when heated, and melt below 140° without further alteration, forming a liquid which solidifies to a glass on cooling. Melezitose is dextro-rotatory ; $[\alpha] = +94{\cdot}1°$. It dissolves easily in water, is nearly insoluble in cold, slightly soluble in boiling alcohol.

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* Comptes Rendus, liii. 1252; liv. 720.

Melezitose decomposes at about 200°. It is carbonised by cold strong sulphuric acid, quickly turns brown with boiling hydrochloric acid, and forms oxalic acid with nitric acid. By an hour's boiling with dilute sulphuric acid, it is converted into glucose. In contact with yeast, it passes slowly, or sometimes not at all, into vinous fermentation. It is not altered at 100° by aqueous alkalis, and scarcely by potassio-cupric tartrate.

Trehalose, $C_{12}H_{22}O_{11}.2H_2O$, is obtained from *Trehala manna*, the produce of a species of Echinops growing in the East, by extraction with boiling alcohol. It forms shining rhombic crystals, containing $C_{12}H_{22}O_{11}.2H_2O$, which melt when quickly heated to 109° ; but if slowly heated give off their water even below 100°. It has a strongly saccharine taste, dissolves easily in water and in boiling alcohol, but is insoluble in ether. The aqueous solution is dextro-rotatory ; $[\alpha] = +199°$.

By several hours' boiling with dilute sulphuric acid, it is converted into dextrose. With strong nitric acid it forms a detonating nitro-compound ; heated with dilute nitric acid it yields oxalic acid. In contact with yeast it passes slowly and imperfectly into alcholic fermentation. It is not altered by boiling with alkalis, and does not reduce cuprous oxide from alkaline cupric solutions. Heated with acetic or butyric acid, it yields compounds not distinguishable from those which are formed in like manner from dextrose (p. 196).

Mycose, $C_{12}H_{22}O_{11}.2H_2O$, is a kind of sugar, very much like trehalose, obtained from ergot of rye by precipitating the aqueous extract of the fungus with basic lead acetate, removing the lead from the filtrate by sulphydric acid, evaporating to a syrup, and leaving the liquid to crystallise. It differs from trehalose only in possessing a somewhat feebler rotatory power ; $[\alpha] = +192{\cdot}5°$, and in not being completely dehydrated at 100°.

Synanthrose, $C_{12}H_{22}O_{11}$, occurs in the tubers of *Dahlia variabilis*, of the Jerusalem artichoke (*Helianthus tuberosus*), and other plants of the composite or synanthraceous order. It is a light amorphous powder, very deliquescent, not sweet, and without action on polarised light. It is resolved by dilute acids or by yeast into dextrose and levulose, and yields saccharic acid by oxidation.

Milk-sugar, Lactin, or **Lactose,** $C_{12}H_{22}O_{11}.H_2O$.—This kind of sugar is an important constituent of milk : it is obtained in large quantities by evaporating *whey* to a syrupy state, and purifying the lactose, which slowly crystallises out, with animal charcoal. It forms white, translucent, four-sided, trimetric prisms, of great hardness. It is slow and difficult of solution in cold water, requiring for that purpose five or six times its weight. Its specific rotatory power in aqueous solution is $[\alpha] = +58{\cdot}3°$. It has a faint, sweet taste, and in the solid state feels gritty between the teeth. When heated, it loses water, and at a high temperature blackens and decomposes. Milk-sugar combines with bases, forming compounds which have an alkaline reaction, and are easily decomposed. Dilute acids convert it into galactose (p. 195).

Milk-sugar, when distilled with oxidising mixtures, such as sulphuric acid and manganese dioxide, yields formic acid. With nitric acid, it forms mucic, saccharic, tartaric, and a small quantity of racemic acid, and finally oxalic acid. Very strong nitric acid, or a mixture of nitric and sulphuric acids, converts milk-sugar into a crystalline substitution-product called nitrolactin.

Milk-sugar is not brought immediately by yeast into the state of alcoholic fermentation; but when it is left for sometime in contact with yeast, fermentation gradually sets in. When cheese or gluten is used as the ferment, the milk-sugar is converted into lactic acid. Alcohol is, however, always formed at the same time, especially if no chalk is added to neutralise the acid as it forms; the quantity of alcohol formed is greater also as the solution is more dilute.

Maltose.—This is a sugar isomeric with lactose, produced by the action of malt-extract on starch. It is less soluble in alcohol than dextrose, has a reducing power about two-thirds as great as that of dextrose, and a specific rotatory power of +56°. By the prolonged action of acids it is converted into dextrose.

OXYGEN-ETHERS OR ANHYDRIDES OF THE POLY-GLUCOSIC ALCOHOLS—AMYLOSES.

These compounds, which are important constituents of the vegetable organism, may be derived from glucose and the poly-glucosic alcohols by abstraction of a molecule of water:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} - H_2O = C_6H_{10}O_5,$$

$$\underset{\substack{\text{Diglucosic}\\\text{alcohol.}}}{C_{12}H_{22}O_{11}} - H_2O = C_{12}H_{20}G_{10}, \text{ or } 2C_6H_{10}O_5,$$

$$\underset{\substack{\text{Triglucosic}\\\text{alcohol.}}}{C_{18}H_{32}O_{16}} - H_2O = C_{18}H_{30}O_{15}, \text{ or } 3C_6H_{10}O_5,$$

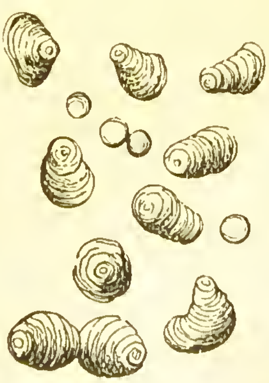
$$\vdots$$

$$C_{6n}H_{10n+2}O_{5n+1} - H_2O = C_{6n}H_{10n}O_{5n}, \text{ or } nC_6H_{10}O_5.$$

All these bodies are therefore isomeric or polymeric one with the other. Their compounds with metallic oxides, &c., have not been sufficiently investigated to fix their exact molecular weight, or to determine in each case the value of *n;* but from the mode of conversion of starch into glucose, and the constitution of certain substitution-products obtained by the action of nitric acid on cellulose, it appears most probable that in these bodies $n = 3$.

Starch, $nC_6H_{10}O_5$, probably $C_{18}H_{30}O_{15}$, also called *Fecula* and *Amidin.*—This is one of the most important and widely diffused of the vegetable proximate principles, being found to a greater or less extent in every plant. It is most abundant in certain roots and tubers, and in soft stems: seeds often contain it in large quantity. From these sources the starch can be obtained by rasping or grinding the vegetable structures to pulp, and washing the mass upon a sieve, by which the torn cellular tissue is retained, while the starch passes through with the liquid, and eventually settles down from the latter, as a soft, white, insoluble powder, which may be washed with cold water, and dried at a very gentle heat. Potatoes treated in this manner yield a large proportion of starch. Starch from grain may be prepared in the same manner, by mixing the meal with water to a paste, and washing the mass upon a sieve: a nearly white, insoluble substance called *gluten* is then left, containing a large proportion of nitrogen. The gluten of wheat-flour is extremely tenacious and elastic. The value of meal as an article of food greatly depends upon this substance. Starch from grain is commonly manufactured on the large scale by steeping the material in water for a considerable time, when the lactic acid, always developed under such circumstances from the sugar of the seed, disintegrates, and in part dissolves the azotised matter, thereby greatly facilitating the mechanical separation of that which remains. A still more easy and successful process has lately been introduced, in which a very dilute solution of caustic soda, containing about 200 grains of alkali to a gallon of liquid, is employed with the same view. Excellent starch is thus prepared from rice. Starch is insoluble in cold water, as indeed its mode of preparation sufficiently shows; it is equally insoluble in alcohol and other liquids, which do not effect its decomposition. To the naked eye it presents the appearance of a soft, white, and often glistening powder: under the microscope it is seen to be altogether destitute of crystalline structure, but to possess, on the contrary, a kind of organisation, being made up of multitudes of little rounded transparent bodies, upon

Fig. 15.



each of which a series of depressed parallel rings, surrounding a central spot or hilum, may often be traced. The starch-granules from different plants vary both in magnitude and form: those from the *Canna coccinea*, or *tous les mois*, and potato being the largest; and those from wheat, and the cereals in general, very much smaller. Figure 15 represents granules of potato-starch, highly magnified.

When a mixture of starch and water is heated to near the boiling-point of the latter, the granules burst and disappear, producing, if the proportion of starch is considerable, a thick gelatinous mass, very slightly opalescent, from the shreds of fine membrane, the envelope of each separate granule. By the addition of a large quantity of water, this gelatinous starch, or *amidin*, may be so far diluted as to pass in great measure through filter-paper. It is very doubtful, however, how far the substance itself is really soluble in water, at least when cold; it is more likely to be merely suspended in the liquid in the form of a swollen, transparent, and insoluble jelly, of extreme tenuity. Gelatinous starch, exposed in a thin layer to a dry atmosphere, becomes converted into a yellowish, horny substance, like gum, which, when put into water, again softens and swells.

Thin gelatinous starch is precipitated by many of the metallic oxides, as lime, baryta, and lead oxide; also by a large addition of alcohol. *Infusion of galls* throws down a copious yellowish precipitate containing tannic acid, which re-dissolves when the solution is heated. By far the most characteristic reaction, however, is that with free *iodine*, which forms with starch a deep indigo-blue compound, which appears to dissolve in pure water, although it is insoluble in solutions containing free acid or saline matter. The colour of the blue liquid is destroyed by heat, temporarily if the heat be quickly withdrawn, and permanently if the boiling be long continued, in which case the compound is decomposed, and the iodine volatilised. Dry starch, put into iodine-water, acquires a purplish-black colour.

The unaltered and gelatinous starch, when dry, have the same empirical formula, $C_6H_{10}O_5$. A compound of starch and lead oxide was found to contain, when dried at 100°, $C_6H_{10}O_5 . PbO$, or $C_{18}H_{30}O_{15} . 3PbO$.

Starch is an important article of food, especially when associated, as in ordinary meal, with albuminous substances. Arrowroot, and the fecula of the *Canna coccinea*, are very pure varieties, employed as articles of diet; arrowroot is obtained from the *Maranta arundinacea*, cultivated in the West Indies; it is with difficulty distinguished from potato-starch.—*Tapioca* is prepared from the root of the *Jatropha Manihot*, being thoroughly purified from its poisonous juice.—*Cassava* is the same substance modified while moist by heat.—*Sago* is made from the soft central portion of the stem of a palm; and *Salep* from the fleshy root of the *Orchis mascula*.

STARCH FROM ICELAND MOSS.—The lichen called *Cetraria Islandica*, purified by a little cold solution of potash from a bitter principle, yields, when boiled in water, a slimy and nearly colourless liquid, which gelatinises on cooling, and dries up to a yellowish amorphous mass, which does not dissolve in cold water, but merely softens and swells. A solution of this substance in warm water is not affected by iodine, although the jelly is turned blue. It is precipitated by alcohol, lead acetate, and infusion of galls, and is converted into glucose by boiling with dilute sulphuric acid. According to Mulder, it contains $C_6H_{10}O_5$. The jelly from certain *algæ*, as that of Ceylon, and the so-called *Carragheen moss*, closely resembles the above.

INULIN.—This substance which differs from common starch in some important particulars, is found in the root of *Inula Helenium*, *Helianthus tuberosus*, *Dahlia*, and several other plants: it may be easily obtained by washing the rasped root on a sieve, and allowing the inulin to settle down from the liquid; or by cutting the root into thin slices, boiling these in water, and filtering while hot; the inulin separates as the solution cools. It is a white, amorphous, tasteless substance, nearly insoluble in cold water, but freely dissolved by the aid of heat; the solution is precipitated by alcohol, but not by acetate of lead or infusion of galls. Iodine colours it brown. Inulin has the same percentage composition as common starch. By boiling with dilute acids, it is completely converted into levulose (p. 193).

Glycogen, $nC_6H_{10}O_5$, was obtained by Bernard from the liver of several animals (calf or pig) by exhaustion with water and precipitating with boiling alcohol. The precipitate is purified by boiling with dilute potash, repeatedly dissolving in strong acetic acid, and precipitating by alcohol. Glycogen also enters largely into the composition of most of the tissues of the embryo. The muscles of fœtal calves of three to seven months have been found to yield from 20 to 50 per cent. of it.

Glycogen is a white, amorphous, starch-like substance, without odour or taste, yielding an opalescent solution with water, but insoluble in alcohol. It does not reduce an alkaline solution of copper. This substance does not ferment with yeast, but is converted into glucose by boiling with dilute acids, or by contact with diastase, pancreatic juice, saliva, or blood.

Dextrin, $C_6H_{10}O_5$.—When gelatinous starch is boiled with a small quantity of dilute sulphuric, hydrochloric, or, indeed, almost any acid, it speedily loses its consistency, and becomes thin and limpid, from having suffered conversion into a soluble gum-like substance, called dextrin, on account of its dextro-rotatory action on polarised light. The experiment is most conveniently made with sulphuric acid, which may be afterwards withdrawn by saturation with chalk. The liquid filtered from the nearly insoluble gypsum may then be evaporated to dryness on a water-bath. The result is a gum-like mass, destitute of crystalline structure, soluble in cold water, precipitable from its solution by alcohol, and capable of combining with lead oxide.

When the boiling with the dilute acid is continued for a considerable time, the dextrin first formed undergoes a further change, and becomes converted into dextro-glucose, which can be thus artificially produced with the greatest facility. The length of time required for this change depends upon the quantity of acid present; if the latter be very small, it is necessary to continue the boiling many successive hours, replacing the water which evaporates. With a larger proportion of acid, the conversion is much more speedy. A mixture of 15 parts of potato-starch, 60 parts water, and 6 parts sulphuric acid, may be kept boiling for about four hours, the liquid neutralised with chalk, filtered, and rapidly evaporated to a small bulk. By digestion with animal charcoal and a second filtration, much of the colour will be removed, after which the solution may be boiled down to a thin syrup, and left to crystallise: in the course of a few days it solidifies to a mass of glucose.

There is another method of preparing this substance from starch which deserves particular notice. Germinating seeds, and buds in the act of development, are found to contain a small quantity of a peculiar azotized substance, called diastase, formed at this particular period from the gluten of vegetable albuminous matter. This substance likewise converts starch into dextrin and glucose, and at a temperature much below the boiling point. When a little infusion of malt, or germinated barley, in tepid water, is mixed with a large quantity of thick gelatinous starch, and the whole kept at about 71°, complete liquefaction takes place in the space of a few minutes, from the production of dextrin and glucose. If a greater degree of heat be employed, the diastase is coagulated and rendered insoluble and inactive. Very little is known respecting diastase itself; it seems very much to resemble vegetable albumin, but has never been obtained in a state of purity.

The change of starch or dextrin into sugar, whether produced by the action of dilute acids or by diastase, takes place quite independently of the oxygen of the air, and is unaccompanied by any secondary product. The acid takes no direct part in the reaction; it may, if not volatile, be all withdrawn without loss after the experiment. The whole reaction lies between the starch and the elements of water, a fixation of the latter occurring in the new product, as will be seen on comparing the composition of starch and glucose. Dextrin itself has exactly the same composition as the original starch.

It was formerly supposed that, in the action of acids [or of diastase] upon starch, the starch is first converted into dextrin by a mere alteration of physical structure, and that the dextrin then takes up the elements of water, and is converted in glucose, this second stage of the process occupying a much longer time than the first; but from the experiments of Musculus* it appears that when the conversion is effected by a dilute acid, both dextrin and glucose are produced at the very commencement of the reaction, and always in the proportion of 1 molecule of glucose to 2 molecules of dextrin: whence it may be inferred that the molecule of starch contains $C_{18}H_{30}O_{15}$, and that it is resolved into glucose and dextrin by taking up a molecule of water:

$$\underset{\text{Starch.}}{C_{18}H_{30}O_{15}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Dextrin.}}{2C_6H_{10}O_5}$$

and that the dextrin, after several hours' boiling, is completely converted into glucose, which is therefore the sole ultimate product of the reaction. When malt extract is used as the converting agent the starch is first resolved into dextrin and maltose (p. 202), in various proportions according to the temperature and other conditions of the reaction; and the dextrin is afterwards very gradually converted into maltose.†

Dextrin is used in the arts as a substitute for gum; it is sometimes made in the manner above described, but more frequently by heating dry potato-starch to 400°, by which it acquires a yellowish tint and becomes soluble in cold water. It is sold in this state under the name of *British Gum.*

Cellulose, $nC_6H_{10}O_5$, probably $C_{18}H_{20}O_{15}$; also called *Lignin.*—This substance constitutes the fundamental material of the structure of plants: it is employed in the organisation of cells and vessels of all kinds, and forms a large proportion of the solid parts of every vegetable. It must not be confounded with *ligneous* or *woody tissue,* which is in reality cellulose with other substances superadded, encrusting the walls of the original membranous cells, and conferring stiffness and inflexibility. Pure cellulose, on the other hand, has the same percentage composition as starch; but woody tissue, even when freed as much as possible from colouring matter and resin by repeated boiling with water and alochol, yields, on analysis, a result indicating an excess of hydrogen above that required to form water with the oxygen, besides traces of nitrogen.

The properties of cellulose may be conveniently studied in fine linen and cotton, which are almost entirely composed of it, the associated vegetable principles having been removed or destroyed by the variety of treatment to which the fibre has been subjected. Pure cellulose is tasteless, insoluble in water and alcohol, and absolutely innutritious: it is not sensibly affected by boiling water, unless it happens to have been derived from a soft or imperfectly developed portion of the plant, in which case it is disintegrated and rendered pulpy. Dilute acids and alkalis exert but little action on cellulose, even at a boiling temperature; strong oil of vitriol converts it, in the cold, into a nearly colourless, adhesive substance, which dissolves in water, and presents the characters of dextrin. This transformation may be conveniently effected by very slowly adding concentrated sulphuric acid to half its weight of lint, or linen cut into small shreds, taking care to avoid any rise of temperature, which would be attended with charring or blackening. The mixing is completed by trituration in a mortar, and the whole left to stand a few hours; after which it is rubbed up with water, warmed, and filtered from a little insoluble matter. The solution may then be neutralised with chalk, and again filtered. The gummy liquid retains lime, partly in the state of sulphate, and partly in combination with sulpholignic acid, an acid composed of the elements of sulphuric acid in union with those of cellulose. If the liquid, previous to neutralisation, be boiled during three or four hours, and the water replaced as it evaporates, the dextrin becomes entirely changed into glucose. Linen rags may, by these means, be made to furnish more than their own weight of that substance.

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* Comptes Rendus, l. 785; liv. 194; Ann. Ch. Phys. [3], lx. 208; [4], v. 177.

† O'Sullivan, Chem. Soc. J. 1876, ii. 125.

If a piece of unsized paper be dipped for a few seconds into a mixture of 2 volumes of concentrated sulphuric acid and 1 volume of water, and then thoroughly washed with water and dilute ammonia, a substance is obtained which resembles parchment, and has the same composition as cellulose; it occurs in commerce under the name of parchment paper (papyrin). An excellent application of this substance in diffusion experiments is mentioned in vol. i. p. 146.

Cellulose dissolves in an ammoniacal solution of cupric oxide (prepared by dissolving basic cupric carbonate in strong ammonia), from which it is precipitated by acids in colourless flakes.

Cellulose is not coloured by iodine.

XYLOÏDIN and PYROXYLIN.—When starch is mixed with nitric acid of specific gravity 1·5, it is converted, without disengagement of gas, into a transparent, colourless jelly, which, when put into water, yields a white, curdy, insoluble substance: this is *xyloïdin.* When dry, it is white and tasteless, insoluble even in boiling water, but freely dissolved by dilute nitric acid, and the solution yields oxalic acid when boiled. Other substances belonging to the same class also yield xyloïdin; paper dipped into the strongest nitric acid, quickly plunged into water, and afterwards dried, becomes in great part so changed: it assumes the appearance of parchment, and becomes highly combustible.

If pure finely divided cellulose, such as cotton-wool, be steeped for a few minutes into a mixture of nitric acid of sp. gr. 1·5 and concentrated sulphuric acid, then squeezed, thoroughly washed, and dried by very gentle heat, it will be found to have increased in weight about 70 per cent., and to have become highly explosive, taking fire at a temperature not much above 149° C. (300° F.), and burning without smoke or residue. This is *pyroxylin*, the *gun-cotton* of Schönbein.

Xyloïdin and pyroxylin are substitution-products consisting of starch and cellulose in which the hydrogen is more or less replaced by nitryl, NO_2. Xyloïdin consists of $C_6H_9(NO_2)O_5$, or $C_{18}H_{27}(NO_2)_3O_{15}$. Of pyroxylin several varieties are known, distinguished by their different degrees of stability and solubility in alcohol, ether, and other liquids. According to Hadow,* the three principal varieties are :—

α.—$C_{18}H_{21}(NO_2)_9O_{15}$, or $C_6H_7(NO_2)_3O_5$, insoluble in a mixture of ether and alcohol, but soluble in ethylic acetate. It is produced by repeated immersion of cotton-wool in a mixture of 2 molecules of nitric acid, HNO_3, 2 molecules of oil of vitrol, H_2SO_4, and 3 molecules of water.

β.—$C_{18}H_{22}(NO_2)_8O_{15}$, soluble in ether-alcohol, insoluble in glacial acetic acid. Produced when the acid mixture contains half a molecule more water than in α.

γ.—$C_{18}H_{23}(NO_2)_7O_{15}$ (Gladstone's *cotton-xyloïdin*), soluble in ether and in glacial acetic acid. Produced when the acid mixture contains one molecule more water than in α.

The first of these, which consists of *trinitrocellulose*, is the most explosive of the three, and the least liable to spontaneous decomposition. It is the only one adapted for use as an explosive agent, and is especially distinguished as "gun-cotton." From the experiments of General von Lenk, of the Austrian service, it appears that, to insure the uniform production of this particular compound the following precautions are necessary :—

1. The cleansing and perfect desiccation of the cotton previously to its immersion in the mixed acids. 2. The employment of the strongest acids procurable in commerce. 3. The steeping of the cotton in a fresh strong mixture of acids after the first immersion and partial conversion into gun-cotton. 4. The continuance of the steeping for forty-eight hours. 5. The thorough purification of the gun-cotton thus produced from every trace of free acid, by washing the product in a stream of water for several weeks ; subsequently a weak solution of potash may be used, but this is not essential.

The solution of the less highly nitrated compounds in alcohol and ether is called collodion. This solution, when left to evaporate, dries up quickly to a thin, transparent, adhesive membrane : it is employed with great advantage in surgery as an air-tight covering for wounds and burns. It is also largely used in photography (i. 87).

Tunicin, $C_6H_{10}O_5$, is a substance closely resembling vegetable cellulose, and perhaps identical therewith, occurring in the mantle of Ascidians (*Cynthia*, *Pallusia*, *&c.*), from which it may be separated by boiling the mantles, first with hydrochloric and then with strong potash-solution, and washing with water. When treated with strong sulphuric acid, it deliquesces to a colourless liquid, which, after boiling with water, is found to contain a glucose.

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* Chem. Soc. Journal, vii. 201.—A series of elaborate and valuable researches on gun-cotton has been published by Abel (Proceed. Royal Soc.) xv. 182; Chem. Soc. Jour. [2], xv. 310.

Gum.—*Gum-arabic*, which is the produce of several species of acacia growing in Egypt and Arabia, may be taken as the type of this class of bodies. When pure, it forms white or slightly yellowish irregular masses, which are destitute of crystalline structure, and break with a smooth conchoïdal fracture. It is soluble in cold water, forming a viscid, adhesive, tasteless solution. It consists of the potassium and calcium salts of arabin or arabic acid, which may be precipitated from the aqueous solution by addition of hydrochloric acid and alcohol, as a white amorphous mass. Arabin, when dried at 100°, has the composition $C_6H_{10}O_5+\frac{1}{2}H_2O$, or $2C_6H_{10}O_5+H_2O$, and is therefore isomeric with cane-sugar ; at 150° it gives off all its water, leaving a residue having the composition $C_6H_{10}O_5$.

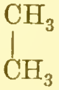
Gum-arabic contains 70·4 per cent. arabin and 17·6 water, the remaining 12 per cent. consisting of metallic salts, silica, iron oxide, &c. Its aqueous solution turns the plane of polarisation to the left, and gives precipitates with basic lead acetate, copper salts, &c. Arabin is oxidised by nitric acid to mucic and saccharic acids. Heated with dilute sulphuric acid, it is converted into a non-fermentable glucose called arabinose, which crystallises in rhombic needles, and exhibits strong dextro-rotation.

Gum Senegal, obtained from a species of acacia growing in Senegal, is very much like gum-arabic, but usually occurs in larger lumps. It contains 81·1 per cent. arabin, 1·6 water, and 2 or 3 per cent. of saline matters. It forms a somewhat stronger mucilage than gum-arabic, and is much used in calico-printing for thickening colours and mordants.

Mucilage, abundant in linseed, in the roots of the mallow, in *salep*, the fleshy root of *Orchis mascula*, and in other plants, differs in some respects from gum-arabic, although it agrees in the property of dissolving in cold water. The solution is less transparent than that of gum, and is precipitated by neutral lead acetate. *Gum-tragacanth*, from *Astragalus verus*, a tree growing in Armenia and the north of Persia, is chiefly composed of a kind of mucilage called *bassorin* ; it does not dissolve in water, but merely softens and assumes a gelatinous aspect. It is dissolved by caustic alkali. *Cerasin* is the insoluble portion of the gum of the cherry-tree ; it resembles bassorin. The composition of these various substances agrees closely with that of starch. Mucilage treated with acids yields dextrose.

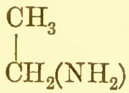
AMINES.

These are compounds which may be derived from hydrocarbons by substitution of the univalent radicle amidogen, NH_2, for an equivalent quantity of hydrogen, or from the alcohols by similar substitution of NH_2 for OH: they are called monamines, diamines, triamines, &c., according to the number of amidogen groups thus introduced: thus from ethane and the corresponding alcohols are derived the following monamine and diamine:



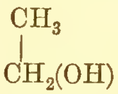
$$\begin{array}{l} CH_3 \\ | \\ CH_3 \end{array}$$

Ethane.



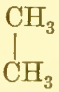
$$\begin{array}{l} CH_3 \\ | \\ CH_2(NH_2) \end{array}$$

Amidethane or Ethylamine.



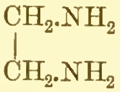
$$\begin{array}{l} CH_3 \\ | \\ CH_2(OH) \end{array}$$

Ethyl alcohol.



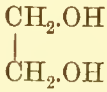
$$\begin{array}{l} CH_3 \\ | \\ CH_3 \end{array}$$

Ethane.



$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array}$$

Diamidethane or Ethene-diamine.

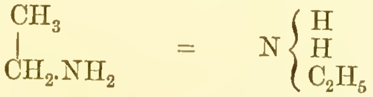


$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

Ethene-alcohol.

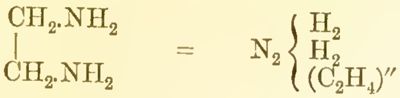
The amines are basic compounds, capable of uniting with acids and forming salts which bear a close resemblance to the salts of ammonia; the amines themselves in the free state are also very much like ammonia, being volatile bodies having a more or less ammoniacal odour and alkaline reaction. They may, in fact, be regarded as derivatives of ammonia, formed by substitution of alcohol-radicles, univalent or multivalent, for an equivalent quantity of hydrogen, in a single, double, or triple molecule of ammonia, NH_3, N_2H_6, N_3H_9, &c., *e.g.*:

Ethylamine,



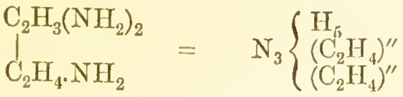
$$\begin{array}{l} CH_3 \\ | \\ CH_2.NH_2 \end{array} = N\left\{\begin{array}{l} H \\ H \\ C_2H_5 \end{array}\right.$$

Ethene-diamine,



$$\begin{array}{l} CH_2.NH_2 \\ | \\ CH_2.NH_2 \end{array} = N_2\left\{\begin{array}{l} H_2 \\ H_2 \\ (C_2H_4)'' \end{array}\right.$$

Diethene-triamine,



$$\begin{array}{l} C_2H_3(NH_2)_2 \\ | \\ C_2H_4.NH_2 \end{array} = N_3\left\{\begin{array}{l} H_6 \\ (C_2H_4)'' \\ (C_2H_4)'' \end{array}\right.$$

MONAMINES.

These bases are derived from a single molecule of ammonia, NH_3. Now this molecule may give up one, two, or all three of its hydrogen-atoms in exchange for univalent alcohol-radicles,—methyl and its homologues, for example,—producing primary, secondary, and tertiary amines. If A, B, C denote three such alcohol-radicles, the amines formed by substituting them for hydrogen in ammonia will be represented by the general formulæ:

$$\underset{\text{Primary.}}{N\left\{\begin{matrix}A\\H\\H\end{matrix}\right.}\qquad\qquad \underset{\text{Secondary.}}{N\left\{\begin{matrix}A\\B\\H\end{matrix}\right.}\qquad\qquad \underset{\text{Tertiary.}}{N\left\{\begin{matrix}A\\B\\C\end{matrix}\right.}$$

In the secondary and tertiary amines the alcohol-radicles denoted by A, B, C may be either the same or different; for example:

$$\overbrace{\underset{\text{Dimethyl-amine.}}{N\left\{\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right.}\quad \underset{\text{Methyl-ethylamine.}}{N\left\{\begin{matrix}CH_3\\C_2H_5\\H\end{matrix}\right.}}^{\text{Secondary}}\quad \overbrace{\underset{\text{Trimethyl-amine.}}{N\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.}\quad \underset{\text{Dimethyl-ethylamine.}}{N\left\{\begin{matrix}CH_3\\CH_3\\C_2H_5\end{matrix}\right.}\quad \underset{\text{Methyl-ethyl-amylamine.}}{N\left\{\begin{matrix}CH_3\\C_2H_5\\C_5H_{11}\end{matrix}\right.}}^{\text{Tertiary.}}$$

The salts of these amines are analogous in composition to the ammonium-salts, and, like the latter, may be regarded either as compounds of ammonia-molecules with acids, or of ammonium-molecules with halogen elements and acid radicles analagous thereto (see p. 25); thus:

$\underset{\text{Ammonia.}}{NH_3} + HCl = NH_4.Cl$, Ammonium chloride.

$\underset{\text{Ethylamine.}}{NH_2(C_2H_5)} + HCl = NH_3(C_2H_5).Cl$, Ethylammonium chloride.

$\underset{\text{Diethylamine.}}{NH(C_2H_5)_2} + HCl = NH_2(C_2H_5)_2.Cl$, Diethylammonium chloride.

$\underset{\text{Triethylamine.}}{N(C_2H_5)_3} + HCl = NH(C_2H_5)_3.Cl$, Triethylammonium chloride.

$\underset{\text{Triethylamine.}}{2N(C_2H_5)_3} + H_2SO_4 = [NH(C_2H_5)_3]_2SO_4$, Triethylammonium sulphate.

All these salts when heated with potash, give off the amine, just as ammonia-salts give off ammonia.

The tertiary amines can unite with the chlorides, &c., of alcohol-radicles in the same manner as with acids: thus triethylamine, $N(C_2H_5)_3$, unites directly with ethyl iodide, C_2H_5I, forming a compound which may be regarded either as *triethylamine ethiodide*, $N(C_2H_2)_3.C_2H_5I$, or as *tetrethylammonium iodide*, $N(C_2H_5)_4I$. Now this iodide, when heated with potash, does not give off ammonia or a volatile ammonia-base; but when heated with silver oxide and water, it is converted, by exchange of iodine for hydroxyl, into a strongly alkaline base, called *tetrethylammonium hydroxide*, which may be obtained in the solid state, and exhibits reactions closely analogous to those of the fixed caustic alkalis. Its formation is represented by the equation:

$$N(C_2H_5)_4I + KOH = KI + N(C_2H_5)_4(OH).$$

Moreover, this base can exchange its hydroxyl for chlorine, bromine, and other acid radicles, just like potash or soda, forming solid crystallisable salts like the iodide above mentioned. These compounds, containing four equivalents of alcohol-radicle, are, in fact, analogous in every respect to ammonium-salts, excepting that the corresponding hydroxides are capable of existing in the solid state, whereas ammonium hydroxide, $NH_4(OH)$, splits up, as soon as formed, into ammonia and water. The radicles $N(C_2H_5)_4$, &c., corresponding with ammonium, are not known in the free state.

The monamines containing more than one carbon-atom are susceptible of isomeric modifications similar to those of the alcohols, and depending on the number of alcohol-radicles in the molecule: thus ethylamine, $CH_2(C_2H_5)$, is isomeric with dimethylamine, $NH(CH_3)_2$; propylamine, $NH_2(C_3H_7)$, is isomeric with methylethylamine, $NH(CH_3)(C_2H_5)$, and with trimethylamine, $N(CH_3)_3$, &c., &c., the number of possible modifications of course increasing with the complexity of the molecules. Moreover, a monamine, either primary, secondary, or tertiary, may admit of modification in the alcohol-radicle itself; thus the primary monamine, $NH_2(C_3H_7)$, may exhibit the two following modifications:

$$\underset{\text{Propylamine.}}{N\left\{\begin{array}{l}CH_2CH_2CH_3\\H\\H\end{array}\right.}\qquad\qquad \underset{\text{Isopropylamine.}}{N\left\{\begin{array}{l}CH(CH_3)_2\\H\\H\end{array}\right.}\quad .$$

General Modes of Formation.—1. By heating the iodides or bromides of the alcohol-radicles to 100° in sealed tubes with alcoholic ammonia. The hydrogen of the ammonia is then replaced by the alcohol-radicle, forming a mixture of primary, secondary, and tertiary amines, which unite with the halogen-acid produced at the same time, to form ammonium salts, thus:

$$NH_3 \quad + \quad \underset{\substack{\text{Ethyl}\\\text{iodide.}}}{C_2H_4I} \quad = \quad \underset{\substack{\text{Ethylammonium}\\\text{iodide.}}}{NH_2(C_2H_5).HI}$$

$$NH_3 \quad + \quad 2C_2H_5I \quad = \quad \underset{\substack{\text{Diethylammonium}\\\text{iodide.}}}{NH(C_2H_5)_2.HI} \quad + \quad HI$$

$$NH_3 \quad + \quad 3C_2H_5I \quad = \quad \underset{\substack{\text{Triethylammonium}\\\text{iodide.}}}{N(C_2H_5)_3.HI} \quad + \quad 2HI$$

From the mixture of ammonium salts thus obtained, the three amines, being volatile, may be at once separated by distillation with aqueous potash or soda:

$$NH_2(C_2H_5).HI \quad + \quad KOH \quad = \quad KI \quad + \quad H_2O \quad + \quad \underset{\text{Ethylamine.}}{NH_2(C_2H_5)}$$

$$NH(C_2H_5)_2.HI \quad + \quad KOH \quad = \quad KI \quad + \quad H_2O \quad + \quad \underset{\text{Diethylamine.}}{NH(C_2H_5)_2}$$

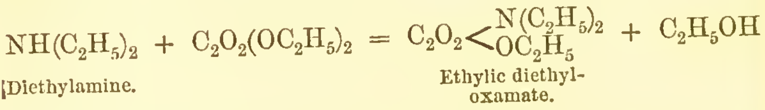
$$N(C_2H_5)_3.HI \quad + \quad KOH \quad = \quad KI \quad + \quad H_2O \quad + \quad \underset{\text{Triethylamine.}}{N(C_2H_5)_3}$$

while the tetrethylammonium iodide remains unaltered, but may be converted into the corresponding hydroxide, $N(C_2H_5)_4OH$, by the action of moist silver oxide in the manner already explained.

The primary, secondary, and tertiary amines cannot be separated by fractional distillation, but their separation may be effected by the following process, devised by Dr. Hofmann. The mixture is treated with diethylic oxalate (oxalic ether), whereby the primary amine is converted into diethyloxamide (see AMIDES), which is easily soluble in water, while the diethylamine is converted into the ethylic ether of diethyloxamic acid, which is insoluble in water, and the triethylamine remains unaltered :

$$2NH_2(C_2H_5) + C_2O_2(OC_2H_5)_2 = C_2O_2(NH.C_2H_5)_2 + 2C_2H_5OH$$

Ethylamine. Diethylicoxalate. Diethyloxamide. Alcohol.



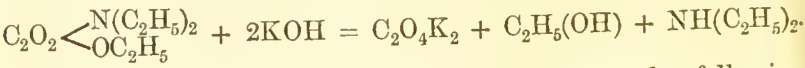
$$NH(C_2H_5)_2 + C_2O_2(OC_2H_5)_2 = C_2O_2\begin{smallmatrix}<N(C_2H_5)_2\\<OC_2H_5\end{smallmatrix} + C_2H_5OH$$

Diethylamine. Ethylic diethyloxamate.

On distilling the product of this reaction, the unaltered triethylamine passes over. From the residue, water extracts the diethyloxamide, which is resolved by boiling with potash into oxalic acid and ethylamine :

$$C_2O_2(NH.C_2H_5)_2 + 2KOH = C_2O_4K_2 + 2NH_2(C_2H_5),$$

and the diethyloxamic ether, which is not dissolved by the water, yields, by distillation with potash, diethylamine :



$$C_2O_2\begin{smallmatrix}<N(C_2H_5)_2\\<OC_2H_5\end{smallmatrix} + 2KOH = C_2O_4K_2 + C_2H_5(OH) + NH(C_2H_5)_2.$$

The primary amines may also be obtained by the following processes :

2. By the action of nascent hydrogen on the nitroparaffins :

$$CH_3.NO_2 + 3H_2 = 2H_2O + CH_3.NH_2$$

Nitromethane. Amidomethane or Methylamine.

3. By the action of nascent hydrogen on the nitrils (azoparaffins, p. 81) :

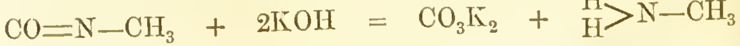
$$HCN + 2H_2 = CH_3.NH_2$$

Formonitril. Methylamine.

$$CH_3.CN + 2H_2 = CH_3.CH_2.NH_2$$

Acetonitril. Ethylamine.

4. By distilling an isocyanic or isocyanuric ether with potash-ley :



$$CO{=}N{-}CH_3 + 2KOH = CO_3K_2 + \begin{smallmatrix}H\\H\end{smallmatrix}{>}N{-}CH_3$$

Methyl isocyanate. Methylamine.

This reaction, which is exactly analogous to the formation of ammonia from cyanic acid, ($CO{=}NH + 2KOH = CO_3K_2 + NH_3$), is that by which the primary amines were first obtained by Wurtz.

Amines are also produced by special reactions, as by the decomposition of more complex nitrogen-compounds and of amido-acids.

Properties and Reactions.—The amines, as already observed, bear a strong resemblance to ammonia. The lower members of the group are gases, easily soluble in water, and having a strong ammoniacal odour; they are distinguished from ammonia by their ready combustibility. The higher members are liquids, more or less oily. Amines expel ammonia from its salts when heated with them, and in like manner the monamines are replaced by the diamines, and these by the triamines: hence it might be inferred that the basic power of an amine increases with the number of alcohol-radicles which it contains; but in this, as in many similar cases, the expulsion of one base or acid by another is a question of relative volatility as well as of strength of combination.

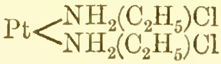
Amines form double salts with *platinic chloride, auric chloride*, and other metallic haloïd salts, exactly similar to those of ammonia, *e.g.:*

Ethylammonium Aurochloride, . .	$NH_3(C_2H_5)Cl.AuCl_3$
Tetramethylammonium Platinochloride,	$2N(C_2H_5)_4Cl.PtCl_4$.

They can also replace ammonia in the alums, and in the salts of platinammonium, cuprammonium, &c. Examples of such compounds are:

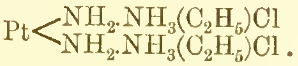
Ethylammonium alum, . . . $(SO_4)_2Al(NH_3.C_2H_5)+12H_2O$

Platosethylammonium chloride, .



$$Pt\begin{cases}NH_2(C_2H_5)Cl\\NH_2(C_2H_5)Cl\end{cases}$$

Platosodiethyldiammonium chloride,



$$Pt\begin{cases}NH_2.NH_3(C_2H_5)Cl\\NH_2.NH_3(C_2H_5)Cl.\end{cases}$$

Primary amines treated with *nitrous acid* (or their haloïd salts with potassium nitrite) are converted into the corresponding alcohols; thus:

$$C_2H_5.NH_2 + NO_2H = N_2 + H_2O + C_2H_5.OH.$$

This reaction—analogous to the resolution of ammonium nitrite into ammonia and water ($NH_3 + NO_2H = N_2 + 2H_2O$)—affords, as already observed (p. 143), the means of passing from one alcohol of a series to the next highest: thus methyl alcohol yields methyl cyanide or formonitril, C_2H_3N; this may be converted by nascent hydrogen into ethylamine, C_2H_7N; and this base, as above, into ethyl alcohol.

Secondary amines are converted by nitrous acid into nitroso-compounds:

$$NH(CH_3)_2 \quad + \quad NO.OH \quad = \quad H_2O \quad + \quad N\left\{\begin{matrix}NO\\CH_3\\CH_3\end{matrix}\right. ;$$

Dimethylamine. Nitroso-dimethylamine.

and tertiary amines are but slightly attacked by nitrous acid.

METHYL BASES.

Methylamine or **Amidomethane,** $CH_5N = H_3C—NH_2 = N\left\{\begin{matrix}H_2\\CH_3\end{matrix}\right.$. This base may be formed by either of the general reactions above given, also by the decomposition of certain natural alkaloïds, as morphine, narcotine, and theine ; but it is best prepared by heating methyl isocyanate with potash in a retort attached to a receiver cooled by a freezing mixture. The distillate, which is an aqueous solution of methylamine, is saturated with hydrochloric acid, and evaporated to dryness, whereby a crystalline residue is obtained consisting of methylammonium chloride; and this when distilled with dry lime yields methylamine in the form of a gas, which must be collected over mercury.

Methylamine is a colourless gas, having an ammoniacal and slightly fishy odour, a specific gravity of 1·08, and condensing to a liquid at $-18°$. It is the most soluble of all gases, one volume of water at 12° absorbing 1040 volumes of the gas : it is likewise very readily absorbed by charcoal. It is distinguished from ammonia by its odour, and by the facility with which it burns. In its deportment with acids and other substances, however, it bears the closest resemblance to ammonia. Its aqueous solution also possesses all the properties of aqueous ammonia, excepting that it does not dissolve the oxides of nickel, cobalt, or cadmium. *Iodine* added to the aqueous solution, throws down a dark red precipitate of di-iodomethylamine, while methylammonium iodide remains in solution:

$$3(CH_3.NH_2) + 2I_2 = CH_3.NI_2 + 2(CH_3.NH_2.HI).$$

Bromine acts in a similar manner. The gas passed over heated potassium is resolved into cyanogen and hydrogen :

$$CH_3.NH_2 + K = CNK + 5H.$$

The salts of methylamine are easily soluble in water. The *hydrochloride*, $CH_5N.HCl$, crystallises in large deliquescent laminæ, which melt at 100°, and distil without decomposition. With platinum chloride it forms a yellow crystalline precipitate of the *platinochloride*, $2(CH_5N.HCl).PtCl_4$, and with auric chloride the double salt, $CH_5N.HCl.AuCl_3$, which crystallises in needles. Methylamine also forms platinum-bases analogous to the ammonio-platinum compounds (i. 512).

Dimethylamine, $C_2H_7N = NH(CH_3)_2$, isomeric with ethylamine, is formed by heating ammonia with methyl iodide, and separated from simultaneously formed methylamine and trimethylamine by means of oxalic ether (p. 214). It is a gas which dissolves easily in water, and condenses to a liquid below +8°. Its platinochloride crystallises in large needles.

Trimethylamine, $C_3H_9N = N(CH_3)_3$, isomeric with propylamine and methyl-ethylamine, is obtained in perfect purity by the action of heat on tetramethyl-ammonium hydroxide, which is thereby completely resolved into trimethylamine and methyl alcohol:

$$N(CH_3)_4OH = N(CH_3)_3 + CH_3(OH).$$

It is also produced by distilling codeine and narcotine with potash, and is contained in large quantity in herring-pickle, the peculiar odour of which is due to its presence. It is a liquid easily soluble in water, and boiling at 9·8°. Its salts are soluble; the hydrochloride very deliquescent.

Tetramethyl-ammonium compounds.—The *iodide*, $N(CH_3)_4I$, may be obtained by adding methyl iodide to trimethylamine. The two substances unite with a sort of explosion. It is more easily prepared, however, by digesting methyl iodide with an alcoholic solution of ammonia. In this reaction a mixture of the iodides of ammonium, methyl-ammonium, dimethyl-ammonium, trimethyl-ammonium, and tetramethyl-ammonium is produced. The first and last compounds are formed in largest quantity, and may be separated by crystallisation, the iodide of tetramethyl-ammonium being but sparingly soluble in water. It crystallises in hard, flat needles of dazzling whiteness. The *hydroxide*, $N(CH_3)_4OH$, resembles the corresponding ethyl-compound (*infra*), and is decomposed by heat, as above mentioned, into methyl alcohol and trimethylamine.

ETHYL-BASES.

Ethylamine or **Amido-ethane,** $C_2H_7N = H_3C - CH_2(NH_2) = N\left\{\begin{matrix}H_2\\C_2H_5\end{matrix}\right.$, is prepared either by heating ethyl isocyanate with potash, or by digesting ethyl bromide or iodide with alcoholic ammonia, and treating the mixture of salts thereby produced with oxalic ether in the manner already described. It is a very mobile liquid, having a specific gravity of 0·6964 at 8°, boiling at 19°, and giving off an inflammable vapour which has a specific gravity of 1·57. It has a most powerful ammoniacal odour, and restores the blue colour to reddened litmus-paper. It produces white clouds with hydrochloric acid, is absorbed by water with great avidity, and reacts like ammonia with metallic salts, precipitating the salts of magnesium, aluminium, iron, manganese, bismuth, chromium, uranium, tin, lead, and mercury; and forming with zinc-salts a white precipitate, which is soluble in excess. It dissolves silver chloride, and yields with copper-salts a blue precipitate, which is soluble in excess of ethylamine.

On adding ethylamine to *oxalic ether*, a white precipitate of diethyloxamide, $C_2O_2(NH.C_2H_5)_2$, is produced. Treated with *chlorine*, it yields ethylammonium chloride and dichlorethylamine, $NCl_2C_2H_5$, a yellow liquid which has a penetrating, tear-exciting odour, and when treated with potash is converted into ammonia, potassium acetate, and potassium chloride:

$$NCl_2(C_2H_5) + 3KHO = C_2H_3KO_2 + 2KCl + NH_3 + H_2O.$$

Ethylamine is decomposed by *nitrous acid*, with formation of ethyl nitrite and evolution of nitrogen:

$$C_2H_7N + 2HNO_2 = C_2H_5NO_2 + 2H_2O + N_2.$$

On passing the vapour of *cyanic acid* into a solution of ethylamine, the liquid becomes hot, and deposits, after evaporation, crystals of ethyl-urea: $C_2H_7N + CNHO = C_3H_8N_2O$ or $CH_3(C_2H_3)N_2O$.

The salts of ethylamine resemble those of ammonia and of methylamine. The *hydrochloride*, $NH_2(C_2H_5).HCl$, crystallises in large deliquescent plates, melting at 80°: the *platinochloride*, $2NH_3(C_2H_5)Cl.PtCl_4$, in orange-yellow scales.

Diethylamine, $C_4H_{11}N = NH(C_2H_5)_2$.—A mixture of the solutions of ethylamine and ethyl bromide, heated in a sealed tube for several hours, solidifies to a crystalline mass of diethylammonium bromide: $NH_2(C_2H_5) + C_2H_5Br = NH_2(C_2H_5)_2Br$. This bromide, distilled with potash, yields diethylamine as a colourless liquid, still very alkaline, and soluble in water, but less so than ethylamine. This compound boils at 57°. It forms beautifully crystallisable salts with acids. A solution of diethyl-ammonium chloride forms with platinic chloride a very soluble double salt, $2NH_2(C_2H_5)_2Cl.PtCl_4$, crystallising in orange-red grains, very different from the orange-yellow leaves of the corresponding ethyl-ammonium salt.

Diethylamine behaves with cyanic acid like ammonia and ethylamine, giving rise to diethyl-urea, $CH_2(C_2H_5)_2N_2O$.

Triethylamine, $C_6H_{15}N = N(C_2H_5)_3$.—The formation of this body is perfectly analogous to that of ethylamine and of diethylamine. On heating for a short time a mixture of diethylamine with ethyl bromide in a sealed glass tube, a beautiful fibrous mass of triethylammonium bromide is obtained, from which the triethylamine may be separated by potash. Triethylamine is a colourless, powerfully alkaline liquid, boiling at 89°. Its salts crystallise remarkably well. With platinic chloride it forms a very soluble double salt, $2NH(C_2H_5)_3Cl.PtCl_4$, which crystallises in magnificent, large, orange-red rhombs.

Tetrethylammonium compounds.—When anhydrous triethylamine is mixed with dry ethyl iodide, a powerful reaction ensues, the mixture boils, and solidifies on cooling to a white crystalline mass of tetrethyl-ammonium iodide: $N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$. This iodide is readily soluble in hot water, from which it separates on cooling in beautiful crystals of considerable size. It is not decomposed by potash, but may be boiled with the alkali for hours without yielding a trace of volatile base. The iodine may, however, be readily removed by treating the solution with silver-salts. If in this case silver sulphate or nitrate be used, we obtain, together with silver iodide, the sulphate or nitrate of tetrethyl-ammonium, which crystallises on evaporation; on the other hand, if the iodide be treated with freshly precipitated silver oxide, the hydroxide of tetrethylammonium, $N(C_2H_5)_4OH$, is separated. On filtering off the silver precipitate, a clear colourless liquid is obtained, which contains the isolated base in solution. It has a strongly alkaline reaction, and intensely bitter taste. The solution of tetrethyl-ammonium hydroxide has a remarkable analogy to potash and soda. Like these substances, it destroys the epidermis and saponifies fatty substances, with formation of true soaps. With metallic salts it exhibits exactly the same reactions as potash. On evaporating a solution of the base in a vacuum, long slender needles are deposited, consisting of the hydroxide with a certain amount of crystallisation-water. After some time these needles disappear, and a semi-solid mass is left, which is the anhydrous base. A concentrated solution of this compound in water may be boiled without decomposition, but on heating the dry substance, it is decomposed into triethylamine, water, and ethene gas:

$$N(C_2H_5)_4(OH) \;=\; H_2O \;+\; N(C_2H_5)_3 \;+\; C_2H_4 .$$

The other salts of tetrethylammonium are obtained by treating the hydroxide with acids: several of them form beautiful crystals. The *platinochloride*, $[N(C_2H_5)_4Cl]_2.PtCl_4$, crystallises in orange-yellow octohedrons, slightly soluble in water, less soluble in alcohol and ether.

The amines of the series $C^nH_{2n+3}N$, which contain more than three atoms of carbon, admit, as already observed, of isomeric modifications, depend on the structure of their alcohol-radicles.

Propylamine (normal), $C_3H_9N = N\left\{\begin{matrix}CH_2CH_2CH_3\\H_2\end{matrix}\right.$, produced by hydrogenation of propionitril (ethyl cyanide), C_3H_5N, or by the action of boiling potash on the mixture of propyl isocyanate and isocyanurate obtained by distilling normal propyl iodide with silver cyanate, is a strongly alkaline liquid, boiling at 50°, and having a specific gravity of 0·7283 at 0°. The *platinochloride*, $2(C_3H_9N.HCl).PtCl_4$, crystalises in orange-yellow monoclinic prisms.

The *nitrite*, $C_3H_9N.NO_2$, is resolved by heat into pseudopropyl alcohol, nitrogen and water, $CH_3—CH_2—CH_2(NH_2) + NO_2H = CH_3—CHOH—CH_3 + N_2 + H_2O$.

Isopropylamine, $CH_3—CH.NH_2—CH_3$, or $N\left\{\begin{matrix}CH(CH_3)_2\\H_2\end{matrix}\right.$, is produced as a formate by the action of hydrochloric acid on isopropyl isocyanide :

$$C{\equiv}N{-}C_3H_7 + 2H_2O = NH_2(C_3H_7).CH_2O_2.$$

The base liberated from this salt by successive treatment with hydrochloric acid and potash, is a sweetish ammoniacal liquid, boiling at 32°. Its platinochloride crystallises in golden-yellow scales or flattened needles.

Butylamines.—Of primary butylamine, $C_4H_{11}N$, there are three modifications, viz. :

1. **Normal Butylamine,** $CH_3.(CH_2)_3.NH_2$, obtained by the action of nascent hydrogen on normal propyl cyanide or butyronitril, $CH_3(CH_2)_2.CN$. It is a colourless, hygroscopic, fuming liquid, boiling at 75·5°, and having a specific gravity of 0·755 at 0°. Nitrous acid converts it into isobutyl alcohol, $CH(CH_3)_2{-}CH_2OH$.

2. **Isobutylamine,** $CH(CH_3)_2.CH_2.NH_2$. is obtained by distilling a mixture of potassium isobutylsulphate with potassium cyanate, and treating the resulting isobutyl isocyanate with potash. It boils at 68°, and has a specific gravity of 0·7357 at 15°. With nitrous acid it yields tertiary butyl alcohol or trimethyl carbonol, $(CH_3)_3.COH$. Now it has been already stated that normal butylamine similarly treated is converted into isobutyl alcohol, and normal propylamine into isopropyl alcohol. Hence it appears that the action of nitrous acid on primary amines gives rise to the alcohol of a radicle containing one more methyl-group than the original amines :

$$\underset{\text{Normal Butylamine.}}{CH_3.CH_2.CH_2.CH_2NH_2} + NO_2H = N_2 + H_2O + \underset{\text{Isobutyl Alcohol.}}{CH(CH_3)_2.CH_2OH}$$

$$\underset{\text{Isobutylamine.}}{CH(CH_3)_2.CH_2.NH_2} + NO_2H = N_2 + H_2O + \underset{\text{Tertiary Butyl alcohol.}}{(CH_3)_3C.COH}$$

3. **Tertiary Butylamine** or **Katabutylamine,** $(CH_3)_3C.NH_2$, is prepared by heating isobutyl iodide with dry silver cyanate, mixing the resulting solid compound of silver iodide and isobutyl cyanate with finely pulverised potassium hydroxide, and distilling the mixture by small quantities at a time. It is a liquid boiling at 45–46°, and having a specific gravity of 0·6987 at 15°.

Dibutylamine, $NH(C_4H_9)_2$, and **Tributylamine,** $N(C_4H_9)_3$, are obtained as bye-products in the preparation of normal valeric acid by the action of alcoholic potash on normal butyl cyanide. The former boils at 160°, the latter between 211° and 215°.

Pentylamines.—Of primary pentylamines, $C_5H_{13}N$, there are two known modifications, viz., isopentylamine or amylamine, derived from the ordinary amyl alcohol of fermentation, and pseudopentylamine, derived from isopropyl-methyl carbinol

(p. 148). They are represented by the following formula:

$$C\left\{\begin{array}{l}CH_2CH(CH_3)_2\\H_2\\NH_2\end{array}\right. \text{ or } N\left\{\begin{array}{l}CH_2CH_2CH(CH_3)_2\\H\\H\end{array}\right. \qquad C\left\{\begin{array}{l}CH(CH_3)_2\\CH_3\\H\\NH_2\end{array}\right. \text{ or } N\left\{\begin{array}{l}CH(CH_3)[CH(CH_3)_2]\\H\\H\end{array}\right.$$

Isopentylamine. Pseudopentylamine.

Isopentylamine or **Ordinary Amylamine**, is obtained by distilling isopentyl isocyanate or isocyanurate, or primary isopentyl-carbamide, $CON_2H_3(C_5H_{11})$, with potash; pseudopentylamine in like manner from secondary isopentyl-carbamide, $CON_2H_2(CH_3)(C_4H_9)$. Both are colourless liquids, of penetrating ammoniacal odour, and slightly soluble in water, to which they impart an alkaline reaction. Amylamine boils at 95°, and has a specific gravity of 0·7503 at 18°; pseudopentylamine boils at 78·5°, and has a specific gravity of 0·755 at 0°. Platinochloride of amylamine crystallises in golden-yellow scales; that of pseudopentylamine in fine crystals derived from a monoclinic prism. The aurochloride of pseudopentyl, $C_5H_{14}N.AuCl_3$, forms large yellow monoclinic crystals.

Diamylamine, $C_{10}H_{23}N = NH(C_5H_{11})_2$.—An aromatic liquid, less soluble in water, and less alkaline than amylamine. It boils at about 170°.

Triamylamine, $C_{15}H_{33}N = N(C_5H_{11})_3$.—A colourless liquid, having properties similar to those of the two preceding bases, but boiling at 257°. The salts of triamylamine are very sparingly soluble in water, and melt, when heated, to colourless liquids, floating upon water.

Tetramylammonium Hydoxide, $C_{20}H_{45}NO = N(C_5H_{11})_4OH$.—This substance is far less soluble than the corresponding bases of the methyl and ethyl series, and separates as an oily layer on adding potash to the aqueous solution. On evaporating the solution in an atmosphere free from carbonic acid, the alkali may be obtained in splendid crystals of considerable size. When submitted to distillation it splits into water, triamylamine, and amylene:

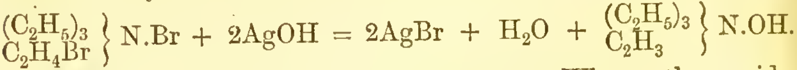
$$N(C_5H_{11})_4OH \quad = \quad H_2O \quad + \quad N(C_5H_{11})_3 \quad + \quad C_5H_{10}.$$

Bromethyl- and Ethenyl- or Vinyl-bases.—Tertiary monamines unite directly with ethene bromide, giving rise to brominated ammonium-bases: *e.g.*,

$$(C_2H_5)_3N \quad + \quad C_2H_4Br \quad = \quad \left.\begin{array}{l}(C_2H_5)_3\\C_2H_4Br\end{array}\right\}N.Br.$$

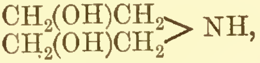
In these compounds, the bromine directly attached to the nitrogen is easily replaceable by double decomposition, by the action of silver nitrate, for example, whereby the bromide is converted into the nitrate $(C_2H_5)_3(C_2H_4Br)N.NO_3$.

The other bromine-atom is more intimately combined, but this also may be removed by the action of moist silver oxide, the group C_2H_4Br or $CH_2Br—CH_2$ being converted, by elimination of HBr, into ethenyl or vinyl $CH_2{=\!=}CH$, and the bromide of triethyl-bromethyl-ammonium being converted into triethyl-vinyl-ammonium hydroxide:



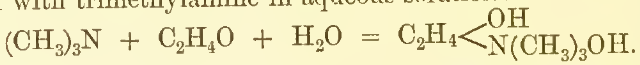
$$\left.\begin{matrix}(C_2H_5)_3\\ C_2H_4Br\end{matrix}\right\}N.Br + 2AgOH = 2AgBr + H_2O + \left.\begin{matrix}(C_2H_5)_3\\ C_2H_3\end{matrix}\right\}N.OH.$$

Oxethene-bases or **Hydramines.**—When etheneoxide, C_2H_4O or $CH_2—O—CH_2$, is treated with aqueous ammonia, 1, 2, or 3 molecules of the oxide unite with 1 mol. ammonia, producing the following bases:

$CH_2(OH)CH_2.NH_2$,	Ethene-hydramine.
 $\begin{matrix}CH_2(OH)CH_2\\ CH_2(OH)CH_2\end{matrix}> NH$,	Diethene-hydramine.
$[CH_2(OH)CH_2]_3N$,	Triethene-hydramine.

The hydrochlorides of these bases are also formed by the action of ammonia on ethene chlorhydrin, $C_2H_4Cl(OH)$. The bases are separated from one another by fractional crystallisation of their hydrochlorides or platinochlorides. They are viscid, alkaline liquids, decomposed by distillation.

Choline, $C_5H_{15}NO_2$.—This base, which has the composition of trimethyl-ethenehydrinammonium hydroxide, $C_2H_4<\begin{matrix}OH\\ N(CH_3)_3OH\end{matrix}$, is formed synthetically by heating ethene oxide or ethene-chlorhydrin with trimethylamine in aqueous solution:

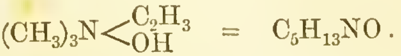


$$(CH_3)_3N + C_2H_4O + H_2O = C_2H_4<\begin{matrix}OH\\ N(CH_3)_3OH.\end{matrix}$$

It exists ready-formed in the animal organism, namely in bile, from which it was first obtained (hence its name); also in the brain, and in white of egg, in both of which it occurs in the form of lecithin, a compound of choline with glycerophosphoric acid and fatty acids. It is also produced from sinapine, the alkaloïd of white mustard, by boiling with alkalis, and is thence also called sincaline.

Choline is a deliquescent substance difficult to crystallise, having a strong acid reaction, and absorbing carbonic acid from the air. Its *platinochloride*, $2(C_5H_{15}NO_2.HCl).PtCl_4$, crystallises in fine red-yellow tables, insoluble in alcohol.

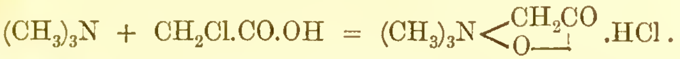
Choline heated with hydriodic acid yields the compound $(CH_3)_3N<\begin{matrix}C_2H_3I\\ I\end{matrix}$, which, by the action of moist silver oxide is converved into trimethyl-vinyl-ammonium hydroxide:



$$(CH_3)_3N<\begin{matrix}C_2H_3\\ OH\end{matrix} = C_5H_{13}NO.$$

This base, called neurine, is very much like choline—from which it differs by H_2O—and likewise exists in the brain.

Betaine, $C_5H_{11}NO_2$, the alkaloid of beet-juice, which has the constitution of trimethyl-glycocine, $(CH_3)_3N{<}\begin{matrix}CH_2.CO\\ O\text{———}\!\mid\end{matrix}$ (see AMIDES), is also nearly related to choline, and is formed by oxidation of choline hydrochloride, whence it is also called oxycholine and oxyneurine. It is formed synthetically, as a hydrochloride, by heating trimethylamine with mono-chloracetic acid:



$$(CH_3)_3N + CH_2Cl.CO.OH = (CH_3)_3N{<}\begin{matrix}CH_2CO\\ O\text{——}\!\mid\end{matrix}.HCl.$$

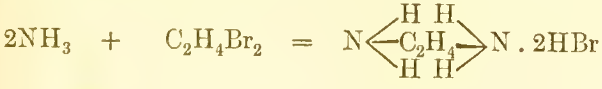
Betaine crystallises from alcohol in shining deliquescent crystals containing one molecule of water. It has a neutral reaction, a sweetish taste, and is decomposed by boiling alkalis, with evolution of trimethylamine.

DIAMINES.

These are bases derived from a double molecule of ammonia, N_2H_6, by substitution of bivalent alcohol-radicles for a part or the whole of the hydrogen, or from the paraffins by substitution of two NH_2-groups for 2 atoms of hydrogen.

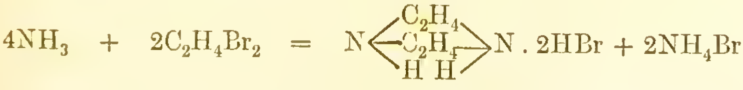
Diamines are formed by the action of ammonia on the chlorides, bromides, and iodides of diatomic alcohol-radicles (olefines).

Ethene-diamines.—By the action of ammonia on ethene dibromide, a number of compounds are produced, among which are the hydrobromides of three bases derived from two molecules of ammonia, by substitution of 1, 2, or 3 molecules of ethene, C_2H_4, for equivalent quantities of hydrogen; thus:



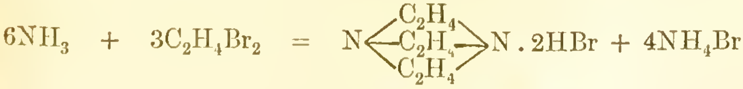
$$2NH_3 + C_2H_4Br_2 = N\left<\begin{matrix}H\ H\\ C_2H_4\\ H\ H\end{matrix}\right>N.2HBr$$

Ethene-diamine.



$$4NH_3 + 2C_2H_4Br_2 = N\left<\begin{matrix}C_2H_4\\ C_2H_4\\ H\ H\end{matrix}\right>N.2HBr + 2NH_4Br$$

Diethene-diamine.



$$6NH_3 + 3C_2H_4Br_2 = N\left<\begin{matrix}C_2H_4\\ C_2H_4\\ C_2H_4\end{matrix}\right>N.2HBr + 4NH_4Br$$

Triethene-diamine.

The mixture of hydrobromides thus obtained is decomposed by distillation with potash, and the three diamines which pass over are separated by fractional distillation.

Ethene-diamine, $C_2H_8N_2 = C_2H_4(NH_2)_2 = N_2\left\{\begin{matrix}C_2H_4\\ H_4\end{matrix}\right.$, is also produced by the action of tin and hydrochloric acid on dicyanogen:

$C_2N_2 + 4H_2 = C_2H_8N_2$. It is a colourless liquid, boiling at 123°, having a strong alkaline reaction, and ammoniacal odour. Nitrous acid converts it into ethene oxide:

$$C_2H_4(NH_2)_2 + N_2O_3 = 2H_2O + 2N_2 + C_2H_4O .$$

Diethene-diamine, $N_2\left\{\begin{matrix}C_2H_4\\C_2H_4,\\H_2\end{matrix}\right.$ boils at 170°; *triethene-diamine*, $N_2(C_2H_4)_3$, at 220°.

These diamines are bi-acid bases, capable of uniting directly with 2 equivalents of an acid. They can also unite with the bromides and iodides of the alcohol-radicles, producing iodides of ammonium bases, thus:

from Ethene-diamine are obtained:

Iodide of Ethene-diammonium, . .	$[N_2H_6(C_2H_4)]I_2$.
Iodide of Diethyl-ethene-diammonium, .	$[N_2H_4(C_2H_4)(C_2H_5)_2]I_2$.
Iodide of Tetrethyl-ethene-diammonium,	$[N_2H_2(C_2H_4)(C_2H_5)_4]I_2$.
Iodide of Pentethyl-ethene-diammonium,	$[N_2H(C_2H_4)(C_2H_5)_5]I_2$.
Iodide of Hexethyl-ethene-diammonium,	$[N_2(C_2H_4)(C_2H_5)_6]I_2$.

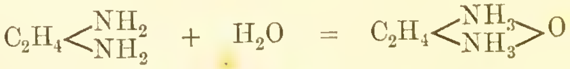
from Diethene-diamine:

Iodide of Diethene-diammonium, . .	$[N_2H_4(C_2H_4)_2]I_2$.
Iodide of Diethyl-diethene-diammonium,	$[N_2H_2(C_2H_4)_2(C_2H_5)_2]I_2$.
Iodide of Triethyl-diethene-diammonium,	$[N_2H(C_2H_4)_2(C_2H_5)_3]I_2$.
Iodide of Tetrethyl-diethene-diammonium,	$[N_2(C_2H_4)_2(C_2H_5)_4]I_2$.

from Triethene-diamine:

Iodide of Diethyl-triethene-diammonium,	$[N_2(C_2H_4)_3(C_2H_5)_2]I_2$.

The diamines also unite directly with water to form ammonium oxides; thus:



$$C_2H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix} + H_2O = C_2H_4{<}\begin{matrix}NH_3\\NH_3\end{matrix}{>}O$$

These oxides are very unstable, and give off the water again on mere distillation over potassium hydroxide: when treated with acids, they form diamine-salts, with separation of water.

Methenyl-diamine, $CN_2H_4 = N_2\left\{\begin{matrix}(CH)'''\\H_3\end{matrix}\right.$, or *Formylimidamide*, $CH{<}\begin{matrix}NH\\NH\end{matrix}$. This base, nearly related to cyanimide or carbodi-imide, $C{<}\begin{matrix}NH\\NH\end{matrix}$, is known only in combination with acids. The *hydrochloride*, $CN_2H_4.HCl$, is produced together with ethyl chloride and ethyl formate, by heating the compound $CNH . HCl$, formed by direct combination of anhydrous hydrocyanic acid and gaseous hydrochloric acid, with alcohol:

$$2(CNH.HCl) + 2(C_2H_5.OH) = CN_2H_4.HCl + C_2H_5Cl + C_2H_5.CHO_2 .$$

It crystallises in needles melting at 81°, and is resolved by alkalis into ammonia and formic acid:

$$CN_2H_4 + 2H_2O = 2NH_3 + CHO.OH.$$

Methyl-methenyl-diamine, Ethenyl-diamine, or **Acediamine,** $C_2N_2H_6 = (H_3C)C\Big\langle\begin{matrix}NH\\NH_2\end{matrix}$. The hydrochloride of this base, $C_2N_2H_6.HCl$, together with acetic acid, is formed by heating acetamide in dry hydrochloric acid gas:

$$2C_2H_5NO_4 + HCl = C_2H_6N_2.HCl + C_2H_4O_2.$$

It crystallises in long needles soluble in water and alcohol. The free base is very unstable, and when separated from the hydrochloride by an alkali, is quickly resolved into ammonia and acetic acid.

Hydroxyl-methenyl-diamine or **Isuret,** $CON_2H_4 = CH\Big\langle\begin{matrix}NH\\NH.OH\end{matrix}$.—This base, isomeric with carbamide, is formed by evaporating an alcoholic solution of hydroxylamine (i. 165) and hydrocyanic acid:

$$CHN + NH^2.OH = CH\Big\langle\begin{matrix}NH\\NH.OH.\end{matrix}$$

It crystallises in rhombic prisms resembling carbamide (urea); melts with partial decomposition at 104°–105°; has an alkaline reaction, and unites with 1 equiv. of acids, forming crystalline salts, which are resolved, on heating their solutions, into formic acid, ammonia, and hydroxylamine. The base itself is also decomposed by boiling its aqueous solution yielding nitrogen, carbon dioxide, ammonia, guanidine, carbamide, and biuret.

TRIAMINES.

Diethene-triamine, $N_4\left\{\begin{matrix}C_2H_4\\C_2H_4\\H_8\end{matrix}\right.$, and **Triethene-triamine,** $N_3\left\{\begin{matrix}(C_2H_4)_3\\H_3\end{matrix}\right.$.—The hydrobromides of these bases are found amongst the products obtained by heating ethene bromide with ammonia. Their formation is represented by the equations,

$$4NH_3 + 2C_2H_4Br_2 = NH_4Br + \underset{\text{Diethene-triamine.}}{N_3(C_2H_4)_2H_5.3HBr}$$

$$6NH_3 + 3C_2H_4Br_2 = 3NH_4Br + \underset{\text{Triethene-triamine.}}{N_3(C_2H_4)_3H_3.3HBr}$$

These bases cannot be separated by distillation, on account of the proximity of their boiling points, but their separation is effected by converting them into platino-chlorides, which crystallise with great facility.

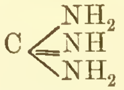
Both these triamines form well-defined crystalline salts, containing 1, 2, and 3 equivalents of acid; and the aqueous solutions of these salts, treated with solid potassium hydroxides, yield the free bases in the form of strongly alkaline oily liquids, soluble in every proportion of water and of alcohol, nearly insoluble in ether. Diethene-triamine boils at 208°, triethene-triamine at 216°.

Triethene Tetramine, $N_4 \left\{ \begin{matrix} (C_2H_4)_3 \\ H_6 \end{matrix} \right.$.—The hydrobromide of this base is also one of the products of the action of ammonia on ethene bromide, but it is more easily obtained by submitting ethene-diamine to the action of ethene bromide:

$$2N_2(C_2H_4)H_4 + C_2H_4Br_2 = N_4(C_2H_4)_3H_6.2HBr.$$

The base, separated from the bromide by silver oxide, is a strongly alkaline liquid, which dries up to a non-crystallising syrup. The *platinochloride*, $N_4(C_2H_4)_3H_6.4HCl.2PtCl_4$, is a pale yellow amorphous, almost insoluble salt.*

Guanidine, CH_5N_3. = **Carbotriamine,** $N_3 \left\{ \begin{matrix} C^{iv} \\ H_5 \end{matrix} \right.$, or **Carbimido-diamide,**



$C \begin{cases} NH_2 \\ NH \\ NH_2 \end{cases}$

.—This base is produced: 1. By the action of aqueous ammonia at 150° on chloropicrin, or on ethyl orthocarbonate:

$$\underset{\text{Chloropicrin.}}{CCl_3(NO_2)} + 3NH_3 = CN_3H_5.HCl + 2HCl + NO_2H.$$

$$\underset{\text{Ethyl Ortho-carbonate.}}{C(OC_2H_5)_4} + 3NH_3 + H_2O = CN_3H_5 + H_2O + 4C_2H_6O.$$

3. By heating cyanamide in alcoholic solution with ammonium chloride:

$$CH_2N_2 + NH_4Cl = CN_3H_5.HCl.$$

4. Together with parabanic acid, by heating guanine (an alkaloid obtained from guano), with a mixture of hydrochloric acid and potassium chlorate, which exerts an oxidising action:

$$C_5H_5N_5O + O_3 + H_2O = CN_3H_5 + C_3N_2H_2O_3 + CO_2.$$

Guanidine, separated from its sulphate by baryta-water, forms colourless crystals, easily soluble in water and alcohol: the solution has a powerful alkaline reaction, and absorbs carbonic acid from the air, forming a carbonate, $2CH_5N_3.H_2CO_3$, which is also alkaline, and crystallises in square prisms.

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* For further details respecting these higher ethene-bases, see Watts's Dictionary of Chemistry, vol. ii. pp. 588–593.

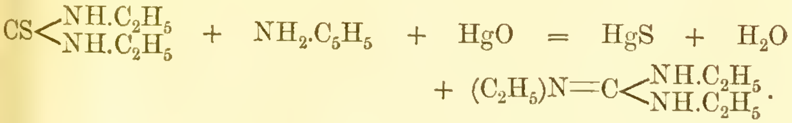
The *nitrate*, $CH_5N_3.NO_3H$, forms large laminæ easily soluble in water. The hydrochloride, $CH_5N_3.HCl$, yields a platino-chloride, crystallising in yellow needles.

Alcoholic derivatives of guanidine are formed by reactions analogous to those which yield guanidine itself, especially by heating cyanamide with the hydrochlorides of primary amines: *e.g.*,

$$CN_2H_2 + NH_2(CH_3).HCl = CN_3H_4(CH_3).HCl.$$

Methyl-guanidine, $CN_3H_4(CH_3)$, is also formed by boiling creatine with water and mercuric oxide. When separated from its hydrochloride by silver oxide it forms a deliquescent crystalline mass, which unites with 1 eq. of acid, forming well-crystallised salts.

Triethyl-guanidine, $CN_3H_2(C_2H_5)_3$, is formed by boiling diethyl-thiocarbamide and ethylamine in alcoholic solution with mercuric oxide:



$$CS{<}\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix} + NH_2.C_5H_5 + HgO = HgS + H_2O + (C_2H_5)N{=}C{<}\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}.$$

The phenyl and tolyl-derivations of guanidine will be described amongst the compounds of the aromatic group; the derivatives containing acid radicles amongst the derivatives of uric acid.

Phosphorus, Arsenic, and Antimony Bases.

Phosphorus, arsenic, and antimony, being like nitrogen, either trivalent or quinquivalent, are capable of forming compounds analogous to the amines and the ammonium salts.

PHOSPHORUS BASES OR PHOSPHINES.

Tertiary phosphines and phosphonium bases are formed by the action of alcoholic iodides on phosphine, PH_3: thus,

$$PH_3 + 3C_2H_5I = 2HI + \underset{\text{Triethyl-phosphine hydriodide.}}{P(C_2H_5)_3.HI.}$$

$$P(C_2H_5)_3 + C_2H_5I = \underset{\text{Triethyl-phosphonium iodide.}}{P(C_2H_5)_4I}$$

or more readily by heating phosphonium iodide, PH_4I (i. 239), to 150°–180° with alcoholic iodides:

$$PH_4I + 3C_2H_5I = 3HI + P(C_2H_5)_3.HI;$$
$$\text{and } P(C_2H_5)_3HI + C_2H_5I = HI + P(C_2H_5)_3I.$$

On heating the product with potash-ley, the hydrodide of the tertiary phosphine is decomposed and the base set free, while the iodide of the phosphonium-base remains unaltered.

The tertiary phosphines are also formed by distilling the zinc-compounds of the alcohol-radicles with phosphorus trichloride in an atmosphere of hydrogen :

$$3Zn(C_2H_5)_2 + 2PCl_3 = 3ZnCl_2 + 2P(C_2H_5)_3.$$

The primary and secondary phosphines are formed by heating the alcoholic iodides with phosphonium iodide to about 150° in presence of certain metallic oxides, such as zinc oxide (ordinary zinc-white of commerce), the product being a mixture of the primary and secondary phosphines :

$$2PH_4I + 2C_2H_5I + ZnO = ZnI_2 + H_2O + 2P(C_2H_5)H_3I$$
$$\text{and } PH_4I + 2C_2H_5I + ZnO = ZnI_2 + H_2O + P(C_2H_5)_2H_2I.$$

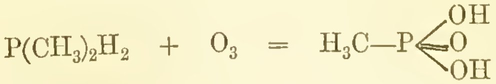
On treating the crystalline product with *water*, monethyl-phosphine is set free :

$$P(C_2H_5)H_3I + H_2O = HI + H_2O + P(C_2H_5)H_2,$$

while the diethylphosphine salt remains unaltered, but may be decomposed by boiling it with caustic soda, the diethylphosphine being then set free.

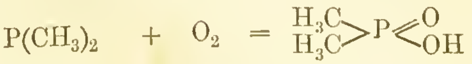
The phosphines are colourless, strongly refracting liquids, having an extremely pungent intoxicating odour. They are nearly insoluble in water. In contact with the air, they oxidise rapidly and mostly take fire : hence their preparation must be conducted in an atmosphere of hydrogen. The salts of the primary phosphines are easily decomposed by water, those of the secondary and tertiary phosphines are not.

The primary phosphines are converted by oxidation into phosphonic acids, those of the secondary phosphines into phosphinic acids (p. 114) : *e.g.*,



$$P(CH_3)_2H_2 + O_3 = H_3C{-}P\begin{cases}OH\\O\\OH\end{cases},$$

Methylphosphonic acid.



$$P(CH_3)_2 + O_2 = \begin{matrix}H_3C\\H_3C\end{matrix}\!>\!P\!<\!\begin{matrix}O\\OH\end{matrix},$$

Dimethyl-phosphinic acid.

The tertiary phosphines unite directly with 1 atom of oxygen, forming neutral oxides, like $(CH_3)_3PO$, and similarly with 1 atom of sulphur, 2 atoms of bromine, iodine, &c., and also with carbon bisulphide.

The following table exhibits the chief distinguishing characters of the methyl and ethyl-phosphines :—

	Boiling Point.	Sp. Gravity.	Hydriodide.	Platino-chloride.
Methyl phosphines:—				
$P(CH_3)H_2$ . . .	Gas liquefying at —14°	...	Thick crystals.	
$P(CH_3)_2H$ . . .	25°	Lighter than water.	...	Crystallises well.
$P(CH_3)_3$ . . .	40°	Lighter than water.		
Ethyl-phosphines:—				
$P(C_2H_5)H_2$ . . .	25°	Lighter than water.	Quadrilateral plates.	
$P(C_2H_5)_2H$ . . .	85°	Lighter than water.	...	Orange-yellow prisms.
$P(C_2H_5)_3$	127°	0·812 at 12°.		Red needles.

The boiling points of the isopropyl, isobutyl, and isopentyl or amyl phosphines are as follows :—

Isopropyl-phosphines, B.P.	$P(C_3H_7)H_2$ 41°	$P(C_3H_7)_2H$ 118°	$P(C_3H_7)_3$ —
Isobutyl-phosphines, B.P.	$P(C_4H_9)H_2$ 62°	$P(C_4H_9)_2H$ 153°	$P(C_4H_9)_3$ 215°
Amyl-phosphines, B.P.	$P(C_5H_{11})H_2$ 106–107°	$P(C_5H_{11})_2H$ 210–215°	$P(C_5H_{11})_3$ 300°

ARSENIC BASES.

Triethylarsine, $As(C_2H_5)_3$, is produced by distilling an alloy of arsenic and sodium with ethyl iodide. At the same time, also, there is formed another body, containing $As_2(C_2H_5)_4$, analogous to arsendimethyl or cacodyl. Both compounds are liquids of powerful odour; they may be separated by distillation in an atmosphere of carbon dioxide, the triethylarsine passing over last.

Triethylarsine may be obtained pure by a process analogous to that employed for the preparation of triethylphosphine, namely, by distilling arsenious chloride, $AsCl_3$, with zinc-ethyl. It is a colourless liquid of most disagreeable odour, similar to that of arsenietted hydrogen, soluble in water, alcohol, and ether, and boiling at 140°. Triethylarsine combines directly with oxygen, sulphur, bromine, and iodine, giving rise to a series of compounds containing 2 atoms of bromine or iodine, 1 atom of sulphur or oxygen, and analogous to the corresponding compounds of triethylstibine.

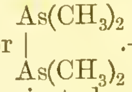
Triethylarsine submitted to the action of ethyl iodide yields a crystalline compound, $As(C_2H_5)_4I$, from which freshly precipitated silver oxide separates the corresponding hydroxide, $As(C_2H_5)_4OH$, a powerfully alkaline substance, similar to the corresponding nitrogen-, phosphorus-, and antimony-compounds.

Analogous substances exist in the methyl series. *Trimethylarsine,*

$As(CH_3)_3$, is formed, together with arsendimethyl or cacodyl, $As_2(CH_3)_4$, when an alloy of arsenic and sodium is submitted to the action of methyl iodide. It unites with methyl iodide, producing *tetramethylarsonium iodide*, $As(CH_3)_4I$, from which silver oxide separates the hydrate, $As(CH_3)_4OH$. The iodide just mentioned is formed, together with iodide of cacodyl, when cacodyl is acted upon by methyl iodide:

$$As_2(CH_3)_4 + 2CH_3I = As(CH_3)_4I + As(CH_3)_2I.$$

By substituting ethyl iodide for methyl iodide in this reaction, the compound $As(CH_3)_2(C_2H_5)_2I$, is formed. All these iodides, treated with moist silver oxide, yield the corresponding hydroxides.



Arsendimethyl or **Cacodyl**, $As_2(CH_3)_4$, or $\begin{array}{l} As(CH_3)_2 \\ | \\ As(CH_3)_2 \end{array}$.—The arsenic in this compound is trivalent, as in those just described, one unit of equivalence of each of the arsenic-atoms being satisfied by combination with the other, just as in the solid hydrogen arsenide, As_2H_4 (i. 452). When, however, the arsendimethyl combines with chlorine or other monatomic radicles, the molecule splits into two; thus:

$$As_2(CH_3)_4 + Cl_2 = 2As(CH_3)_2Cl.$$

Cacodyl, so called from its repulsive odour, constitutes, together with its products of oxidation, the spontaneously inflammable liquid known as *Cadet's fuming liquid*, or *Alkarsin*. This liquid is prepared by distilling equal weights of potassium acetate and arsenious oxide in a glass retort connected with a condenser and tubulated receiver cooled by ice, a tube being attached to the receiver to carry away the permanently gaseous products to some distance from the experimenter. At the close of the operation, the receiver is found to contain two liquids, besides a quantity of reduced arsenic: the heavier of these is the crude cacodyl; the other consists chiefly of water, acetic acid, and acetone. The gas given off during the distillation is principally carbon dioxide. The crude cacodyl is repeatedly washed by agitation with water previously freed from air by boiling, and afterwards redistilled from potassium hydrate in a vessel filled with pure hydrogen gas. All these operations must be conducted in the open air.

Pure cacodyl is obtained by decomposing the chloride with metallic zinc, dissolving out the zinc chloride with water, and dehydrating the oily liquid with calcium chloride. The strong tendency of cacodyl to take fire in the air, and the extremely poisonous character of its vapour, render it necessary to perform all the distillations in sealed vessels filled with carbon dioxide.

Cacodyl is a colourless, transparent liquid, boiling at 170°, and crystallising at 6° in large transparent prisms. It smells like alkarsin, and is even more inflammable. At a temperature below redness it is resolved into metallic arsenic and a mixture of 2 vols. methane and 1 vol. ethene: $2As_2C_2H_6 = As_4 + 2CH_4 + C_2H_4$.

Cacodyl instantly takes fire when poured out into air or oxygen or chlorine. With very limited access of air it throws off white fumes, passing into oxide and ultimately into cacodylic acid: it combines also directly with sulphur. It can take up 2 atoms of a monad or 1 atom of a dyad element, forming compounds like the chloride, $As_2(CH_3)_4Cl_2 = 2As(CH_3)_2Cl$, and the oxide, $As_2(CH_3)_4O$, in which the arsenic is trivalent; or again, 6 atoms of a monad or 3 atoms of a dyad element, forming compounds like the trichloride, $As_2(CH_3)_4Cl_6 = 2As(CH_3)_2Cl_3$, in which the arsenic is quinquivalent. These last mentioned bodies are the most stable of all the cacodyl compounds.

Cacodyl Chloride or *Arsen-chlorodimethide*, $As(CH_3)_2Cl$, is obtained by distilling alkarsin with strong hydrochloric acid, or better, by mixing the dilute alcoholic solutions of alkarsin and mercuric chloride, distilling the resulting precipitate of cacodylic chloromercurate, $As_2(CH_3)_4O.2HgCl_2$, with very strong hydrochloric acid, and digesting the distillate for several days in a sealed bulb apparatus with calcium chloride and quicklime, and finally distilling it in an atmosphere of carbon dioxide.

Cacodyl chloride is a colourless liquid which does not fume in the air, but emits an intensely poisonous vapour. It is heavier than water, insoluble in that liquid and in ether, but easily soluble in alcohol. The boiling point of this compound is a little above 100°; its vapour is colourless, spontaneously inflammable in the air, and has a density of 4·56. Dilute nitric acid dissolves the chloride without change; with the concentrated acid ignition and explosion occur. Cacodyl chloride combines with cuprous chloride, forming a white, insoluble, crystalline double salt, containing $As_2(CH_3)_4Cl_2.Cu_2Cl_2$; also with cacodyl oxide. It forms a thick, viscid hydrate, easily dehydrated by calcium chloride. *Cacodyl trichloride*, $As(CH_3)_2Cl_3$, is produced by the action of phosphorus pentachloride on cacodylic acid:

$$As(CH_3)_2O(OH) + 2PCl_5 = As(CH_3)_2Cl_3 + 2POCl_3 + HCl;$$

also by the action of chlorine gas on the monochloride. Prepared by the first method, it forms splendid large prismatic crystals, which are instantly decomposed, between 40° and 50°, into methyl chloride and arsen-monomethyl chloride:

$$As(CH_3)_2Cl_3 = CH_3Cl + As(CH_3)Cl_2.$$

Cacodyl Iodide, $As(CH_3)_2I$, is a thin, yellowish, heavy liquid, of offensive odour, prepared by distilling alkarsin with strong solution of hydriodic acid. A yellow crystalline oxyiodide is formed at the same time. *Cacodyl bromide* and *fluoride* have also been obtained.

Cacodyl Cyanide, $As(CH_3)_2CN$, is easily formed by distilling alkarsin with strong hydrocyanic acid, or mercuric cyanide. Above

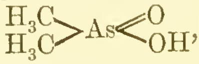
33° it is a colourless, ethereal liquid, but below that temperature it crystallises in colourless four-sided prisms, of beautiful diamond lustre. It boils at about 140°, and is but slightly soluble in water. It takes fire only when heated. The vapour of this substance is most fearfully poisonous: the atmosphere of a room is said to be so far contaminated by the evaporation of a few grains of it as to cause instantaneous numbness of the hands and feet, vertigo, and even unconsciousness.

Cacodyl Oxide, $As_2(CH_3)_4O$, is formed by the slow oxidation of cacodyl. When air is allowed access to an aqueous solution of alkarsin, so slowly that no sensible rise of temperature follows, that body is gradually converted into a thick, syrupy liquid, full of crystals of cacodylic acid. On dissolving this mass in water, and distilling, water having the odour of alkarsin passes over, and afterwards an oily liquid, which is the cacodyl oxide. Impure cacodylic acid remains in the retort.

Cacodyl oxide, purified by rectification from caustic baryta, is a colourless, oily liquid, having a pungent odour, sparingly soluble in water, solidifying at −25°, and boiling at 150°. It strongly resembles alkarsin in odour, in its relations to solvents, and in the greater number of its reactions; but it neither fumes in the air, nor takes fire at common temperatures: its vapour mixed with air, and heated to about 88°, explodes with violence. It dissolves in hydrochloric, hydrobromic, and hydriodic acids, forming chloride, bromide, and iodide of cacodyl.

Cacodyl dioxide, $As_2(CH_3)_4O_2$, is the thick syrupy liquid produced by the slow oxidation of cacodyl or of alkarsin. It is decomposed by water, and then yields a distillate of cacodyl monoxide, with a residue of cacodylic acid:

$$2As_2(CH_3)_4O_2 + H_2O = As_2(CH_3)_4O + 2As(CH_3)_2O(OH).$$

Cacodylic or *Dimethyl-arsenic Acid*,  $\begin{matrix}H_3C\\H_3C\end{matrix}\!>As\!<\!\begin{matrix}O\\OH\end{matrix}$, also called *Alkargen*.—This is the ultimate product of the action of oxygen at a low temperature upon cacodyl or alkarsin in presence of water: it is best prepared by adding mercuric oxide to alkarsin, covered with a layer of water and artificially cooled, until the mixture loses all odour, and afterwards decomposing any mercuric cacodylate that may have been formed, by the cautious addition of more alkarsin. The liquid yields, by evaporation to dryness and solution in alcohol, crystals of cacodylic acid. The sulphide and other compounds of cacodyl yield the same substance on exposure to air. Cacodylic acid forms brilliant, colourless, brittle crystals, which have the form of a modified square prism: it is permanent in dry air, but deliquescent in a moist atmosphere. It is not at all poisonous, though it contains more than 50 per cent. of arsenic. It is very soluble in water and in alcohol, but not in ether: the solution has an acid reaction. When mixed with alkalis and evaporated, it leaves a gummy amorphous mass. With the oxides of silver and mercury, on the other hand, it yields crystallisable compounds. It unites with cacodyl oxide, and forms a variety of combinations with metallic salts. Cacodylic acid is exceedingly stable: it is not affected by red fuming nitric acid, nitromuriatic acid, or even chromic acid in solution: it may be boiled with these substances without the least change. It is deoxidised, however, by phosphorous acid and stannous chloride, yielding cacodyl oxide. Dry hydriodic acid gas decomposes it, with production of water, cacodyl iodide, and free iodine. With dry hydrochloric acid gas, or with the concentrated aqueous acid, cacodylic acid unites directly, forming the compound $As(CH_3)_2O_2H.HCl$. But by exposing cacodylic acid for a long time to a stream of hydrochloric acid gas, arsen-monomethyl dichloride is obtained, together with water and methyl chloride:

$$As(CH_3)_2O_2H + 3HCl = As(CH_3)Cl_2 + 2H_2O + CH_3Cl.$$

Phosphorus pentachloride converts cacodylic acid into cacodylic trichloride (p. 231).

Cacodyl Sulphide, $As_2(CH_3)_4S$, is formed by adding barium sulphide to crude cacodyl, or by distilling barium sulphydrate with cacodyl chloride. It is a transparent liquid which retains its fluidity at −40°, and boils at a temperature considerably above 100°.

Cacodyl disulphide, $As_2(CH_3)_4S_2$, is formed by the action of sulphur on cacodyl or the monosulphide, or by treating cacodylic acid with sulphuretted hydrogen in a vessel externally cooled. It separates from the solution in large rhombic crystals. Its alcoholic solution yields with various metallic solutions, precipitates consisting of salts of thiocacodylic acid, $As(CH_3)_2S(SH)$, analogous to cacodylic acid. The lead salt, $As_2(CH_3)_4S_4Pb$, forms small white crystals.

Arsenmonomethyl, $As(CH_3)$.—This radicle, which is not known in the separate state, is either bivalent or quadrivalent. Its *dichloride*, $As(CH_3)Cl_2$, is produced either by the decomposition of cacodyl trichloride by heat: $As(CH_3)_2Cl_3 = As(CH_3)Cl_2 + CH_3Cl$; or by the prolonged action of hydrochloric acid on cacodylic acid. It is a colourless, heavy mobile liquid, having a strong reducing power; it boils at 133°. Its vapour exerts a most violent action on the mucous membranes; on smelling it, the eyes, nose, and whole face swell up, and a peculiar lancinating pain is felt, extending down to the throat. The *tetrachloride*, $As(CH_3)Cl_4$, is obtained in large crystals by passing chlorine over a mixture of the dichloride and carbon bisulphide cooled to −10°. It is very unstable, decomposing even near 0° into methyl chloride and arsenious chloride, $AsCl_3$. There is also a chlorobromide, $As(CH_3)ClBr$, and a di-iodide, $As(CH_3)I_2$.

The *oxide*, $As(CH_3)O$, obtained by decomposing the dichloride with potassium carbonate, forms large cubical crystals, soluble in water, alcohol, and ether, and resolved by distillation with potash into arsenious oxide and cacodyl oxide: $4As(CH_3)O = As_2O_3 + As_2(CH_3)_4O$.

Arsenmethylic Acid, $As(CH_3)O(OH)_2$, is obtained as a barium-salt by decomposing arsenmethyl dichloride with a slight excess of silver-oxide; and this salt, decomposed by sulphuric acid, yields the acid, which remains on evaporation in the form of a laminated mass. It is bibasic.

Arsenmethyl sulphide, $As(CH_3)S$, is obtained as a white mass by passing hydrogen sulphide over the dichloride.

On comparing the combining or equivalent values of the several arsenides of methyl, it will be seen that they all unite with elementary bodies and compound radicles, in such proportions as to form compounds in which the arsenic is either trivalent or quinquivalent, the last-mentioned compounds being by far the most stable. Thus:

Arsenmonomethyl, $As(CH_3)$, is bi- and quadri-valent, forming the chlorides $As(CH_3)Cl_2$ and $As(CH_3)Cl_4$.

Arsendimethyl, $As(CH_3)_2$, is uni- and tri-valent, forming the chlorides $As(CH_3)_2Cl$ and $As(CH_3)_2Cl_3$.

Arsentrimethyl, $As(CH_3)_3$, is bivalent only, and forms the chloride $As(CH_3)_3Cl_2$.

Arsentrimethylium, or Tetramethylarsonium, $As(CH_3)_4$, is univalent, forming the chloride $As(CH_3)_4Cl$.

ANTIMONY-BASES OR STIBINES.

Of these only the tertiary bases and the corresponding stibonium-compounds are known.

Triethylstibine or **Stibethyl**, $Sb(C_2H_5)_3$, is obtained by distilling ethyl iodide with an alloy of antimony and potassium. It is a transparent, very mobile liquid, having a penetrating odour of onions. It boils at 158°. In contact with atmospheric air, it emits a dense white fume, and frequently even takes fire, burning with a white brilliant flame. It is analogous in many of its reactions to triethylamine, but has much more powerful combining tendencies, uniting readily with 2 atoms of chlorine, bromine, or iodine, and 1 atom of oxygen or sulphur, thereby forming compounds in which the antimony is quinquivalent, such as $Sb(C_2H_5)_3Cl_2$, $Sb(C_2H_5)_3O$, &c. The same tendency to act as a bivalent-radicle is, however, exhibited by triethylamine, which, though it does not unite directly with elementary bodies, can nevertheless take up a molecule of hydrogen chloride, ethyl iodide, &c., likewise producing compounds in which the nitrogen is quinquivalent, *e.g.*,

$$N(C_2H_5)_3HCl, \quad N(C_2H_5)_3(C_2H_5)I, \ \&c.$$

Stibethyl oxide, $Sb(C_2H_5)_3O$, forms a viscid, transparent, bitter, non-poisonous mass, soluble in water and alcohol; not volatile without decomposition. Treated with acids, it forms crystallisable salts containing 2 molecules of a monatomic or 1 molecule of a diatomic acid radicle, *e.g.:* $Sb(C_2H_5)_3(NO_3)_2$, $Sb(C_2H_5)_3SO_4$, &c. The *sulphide*, $Sb(C_2H_5)_3S$, forms beautiful crystals of silvery lustre, soluble in water and alcohol. Their taste is bitter, and their odour similar to that of mercaptan. The solution of this compound exhibits the deportment of an alkaline sulphide: it precipitates metals from their solutions as sulphides, a soluble salt of stibethyl being formed at the same time. This deportment, indeed, affords the simplest means of preparing the salts of stibethyl. The *chloride*, $Sb(C_2H_5)_3Cl_2$, is a colourless liquid, having the odour of turpentine oil. The *iodide*, $Sb(C_2H_5)_3I_2$, forms colourless needles of intensely bitter taste.

The analogy of triethylstibine to triethylamine is best exhibited in its deportment with ethyl iodide. The two substances combine, forming tetrethylstibonium iodide, $Sb(C_2H_5)_4I$, from which silver oxide separates a powerful alkaline base analogous to tetrethylammonium hydroxide:

$$N(C_2H_5)_4(OH) \qquad\qquad Sb(C_2H_5)_4OH\,.$$

A series of analogous substances exists in the methyl series. They have been examined by Landolt, who has described several of their compounds, and separated the methyl-antimony-base analogous to tetramethylammonium hydrate.

The *iodide*, $Sb(CH_3)_4I$, produced by the action of methyl iodide upon trimethylstibine, $Sb(CH_3)_3$, crystallises in white six-sided tables, which are easily soluble in water and alcohol, and slightly soluble in ether. It has a very bitter taste, and is decomposed by the action of heat. When treated with silver oxide, it yields a powerfully alkaline solution, exhibiting all the properties of potash, from which, on evaporation, a white crystalline mass, the *hydroxide of tetramethylstibonium*, $Sb(CH_3)_4(OH)$, crystallises. This compound forms an acid sulphate, $Sb(CH_3)_4SO_4H$, which crystallises in tables.

Bismethyl or **Triethylbismuthine**, $Bi(C_2H_5)_3$, analogous in composition to triethylstibine and triethylarsine, is formed by the action of ethyl iodide on an alloy of bismuth and potassium, and is extracted from the residue by ether. It is a yellow liquid of specific gravity 1·82, has a most nauseous odour, and emits vapours which take fire in contact with the air. It unites with oxygen, chlorine, bromine, iodine, and nitric acid.

DIATOMIC BASES OF THE PHOSPHORUS AND ARSENIC SERIES.

The action of ethene bromide on triethylphosphine gives rise to the formation of two crystalline bromides, according to the proportions in which the substances are brought in contact. These bromides are $C_8H_{19}PBr_2 = (C_2H_5)_3P + C_2H_4Br_2$ and $C_{14}H_{34}P_2Br_2 = 2(C_2H_5)_3P + C_2H_4Br_2$. The first of these compounds is the bromide of a phosphonium in which 3 atoms of hydrogen are replaced by ethyl and 1 atom by the univalent radicle bromethyl, C_2H_4Br, namely, $[(C_2H_4Br)(C_2H_5)_3P]Br$. Half the bromine in this salt is unaffected by the action of silver-salts; it may accordingly be designated as *bromide of bromethyl-triethyl-phosphonium*. Numerous salts of this compound are known, but the free base cannot be obtained, since silver oxide eliminates the latent bromine, giving rise to the formation of a base containing $[C_2H_5O)(C_2H_5)_3P]OH$. The second compound is the dibromide of *ethene-hexethyl-diphosphonium*, $[(C_2H_4)(C_2H_5)_6P_2]Br_2$. This radicle, analogous to diammonium, N_2H_8, forms a series of very stable and beautiful salts, especially an iodide, which is difficultly soluble in water. In all these salts the base, which is composed of 1 atom of ethene, 6 atoms of ethyl, and 2 atoms of phosphorus, is united with 2 equivalents of univalent acid radicle; the platinum-salt contains $(C_2H_4)(C_2H_5)_6P_2Br_2PtCl_4$. The very caustic and stable base has the composition $[(C_2H_4)(C_2H_5)_6P_2](OH)_2$.

The dibromide of ethene-hexethyl-diphosphonium may be formed by the action of triethylphosphine upon the brominated bromide which has been mentioned as the first product of the action of ethene dibromide upon triethylphosphine: $C_8H_{19}PBr_2.(C_2H_5)_3P = C_{14}H_{34}P_2Br_2$. If the triethylphosphine be replaced in this process by ammonia or by monamines in general, or by monarsines, an almost unlimited series of diatomic salts may be formed, in which phosphorus and nitrogen or phosphorus and arsenic are associated.

Thus the action of ammonia, of ethylamine, and of triethylarsine, gives rise respectively to the following compounds:

Dibromide of Ethene-triethyl-phosphammonium, . . .	$[(C_2H_4)(C_2H_5)_3H_3PN]Br_2$.
Dibromide of Ethene-tetrethyl-phosphammonium, . . .	$[(C_2H_4)(C_2H_5)_4H_2PN]Br_2$.
Dibromide of Ethene-hexethyl-phospharsonium, ...	$[(C_2H_4)(C_2H_5)_6PAs]Br_2$.

Treated with silver oxide those bromides yield the very caustic diatomic bases—

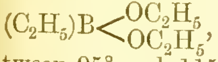
Hydroxide of Ethene-triethyl-phosphammonium, . . .	$[(C_2H_4)(C_2H_5)_3H_3PN](OH)_2$.
Hydroxide of Ethene-tetrethyl-phosphammonium, . . .	$[(C_2H_4)(C_2H_5)_4H_2PN](OH)_2$.
Hydroxide of Ethene-hexethyl-phospharsonium, ...	$[(C_2H_4)(C_2H_5)_6PAs](OH)_2$.

The arsenic bases, when submitted to the action of ethene dibromide, give rise to perfectly analogous results. The limits of this Manual will not premit us to examine these compounds in detail.

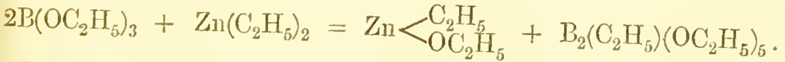
ORGANO-BORON COMPOUNDS.

Boric Triethide or **Borethyl**, $B(C_2H_5)_3$, discovered by Frankland, is obtained, together with zinc-ethoxide, by treating triethylic borate with zinc-ethide:

$$B(OC_2H_5)_3 + 3Zn(C_2H_5)_2 = 3Zn(OC_2H_5)_2 + B(C_2H_5)_3.$$

It is a colourless, mobile liquid, having a pungent odour, irritating the eyes, of sp. gr. 0·696 at 23°, and boiling at 95°. Borethyl is insoluble in water, but very slowly decomposed when left in prolonged contact with it. When exposed to the air it takes fire, burning with a beautiful green and somewhat smoky flame. It combines with ammonia, forming the compound $NH_3.B(C_2H_5)_3$. By the gradual action of dry air, and, ultimately of dry oxygen, borethyl is converted into the diethylic ether of ethylboric acid,  $(C_2H_5)B{<}{\substack{OC_2H_5\\OC_2H_5}}$, a liquid boiling, with partial decomposition, between 95° and 115°, but distilling unchanged under reduced pressure. In contact with water this liquid is immediately transformed into ethylboric acid, $(C_2H_5)B(OH)_2$.

*Diboric Ethopentethoxide** (or Ethopentethylate), $B_2(C_2H_5)(OC_2H_5)_5$, is formed by heating 2 molecules of boric ether with 1 molecule of zinc ethide:



$$2B(OC_2H_5)_3 + Zn(C_2H_5)_2 = Zn{<}{\substack{C_2H_5\\OC_2H_5}} + B_2(C_2H_5)(OC_2H_5)_5.$$

It is a colourless, mobile liquid, boiling at about 120°, and condensing unchanged. Its vapour-density, taken between 114° and 120°, is 69 ($H = 1$), which represents a four-volume condensation, indicating that the compound, in passing from the liquid to the gaseous state, is broken up into diethylic ethylborate and boric ether:

$$B_2(C_2H_5)(OC_2H_5)_5 = (C_2H_5)B(OC_2H_5)_2 = B(OC_2H_5)_3,$$

just as sal-ammoniac, NH_4Cl, is resolved by heat into NH_3 and HCl, which together occupy four volumes of vapour (i. 253). A similar deportment is exhibited by ammonioboric methide, $NH_3.B(CH_3)_3$, which is resolved by heat into NH_3 and $B(CH_3)_3$, the mixed vapour resulting from the decomposition having also a four-volume condensation. These results render it probable that the compounds under consideration have a constitution analogous to that of the ammonium salts, and that boron, though generally triadic, may, like nitrogen, enter into combination also as a pentad. On this view the constitution of ammonioboric methide and diboric ethopentethoxide may be represented by the following formulæ:

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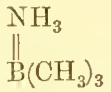
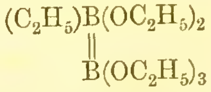
* This and the following compounds have quite recently been discovered by Frankland (Proc. Roy. Soc. 1876, vol. xxv. p. 165).



$$\begin{matrix} NH_3 \\ \| \\ B(CH_3)_3 \end{matrix}$$

Ammonioboric methide.



$$\begin{matrix} (C_2H_5)B(OC_2H_5)_2 \\ \| \\ B(OC_2H_5)_3 \end{matrix}$$

Diboric Ethopentethoxide.

In contact with water diboric ethopentethoxide is immediately decomposed into boric acid, ethyl-boric acid, and alcohol:

$$B_2(C_2H_5)(OC_2H_5)_5 + 5H_2O = B(OH)_3 + (C_2H_5)B(OH)_2 + 5C_2H_5(OH).$$

Boric Diethylethoxide, $(C_2H_5)_2B(OC_2H_5)$, is produced by boiling boric ether with 2 molecules of zinc ethide:

$$B(OC_2H_5)_3 + 2Zn(C_2H_5)_2 = 2Zn\Big\langle\begin{matrix}C_2H_5\\OC_2H_5\end{matrix} + (C_2H_5)_2B(OC\ H_5).$$

When purified by distillation in an atmosphere of carbon dioxide, it is a colourless, mobile pungent liquid boiling at 102°, and having (at 135·5°) a vapour-density of 56·5 (H=1), indicating a normal two-volume condensation. It takes fire in the air, and burns with a green flame. Exposed to dry air and then to oxygen, it oxidises to boric ethylodiethoxide, $(C_2H_5)B(OC_2H_5)_2$.

Boric Diethylhydroxide, $(C_2H_5)_2B(OH)$, formed by agitating boric diethyl-ethoxide with water, is a spontaneously inflammable ethereal liquid, resembling boric ethide, and decomposing when distilled.

Boric Ethyl-hydroxethoxide, $(C_2H_5)B\Big\langle\begin{matrix}OC_2H_5\\OH\end{matrix}$, is formed by exposing the last compound in a cooled vessel to a slow current of dry air. It is liquid at ordinary temperatures, but solidifies below 8° to a white crystalline body smelling like borethide, and having a pungent taste. It is rapidly decomposed by water into ethylboric acid and alcohol:

$$(C_2H_5)B(OH)(OC_2H_5 + H_2O = (C_2H_5)B(OH)_2 + C_2H_5OH.$$

It is not spontaneously inflammable, and cannot be distilled under ordinary atmospheric pressure without decomposition.

Boric Trimethide or **Bor-methyl**, $B(CH_3)_3$, obtained like ethyl-compound, is a colourless gas, which condenses to a liquid at low temperatures. It unites with ammonia, forming the compound $H_3N{=}B(CH_3)_3$.

ORGANO-SILICON COMPOUNDS.

Silicon is a tetrad element, and forms with alcohol-radicles compounds bearing a very close analogy to the hydrocarbons.

Silicic-Tetramethide, $Si(CH_3)_4$, is produced by heating silicon tetrachloride with zinc methide:

$$SiCl_4 + 2Zn(CH_3)_2 = 2ZnCl_2 + Si(CH_3)_4.$$

It is a mobile liquid, which boils at 30°, is not decomposed by water, and reacts generally like a hydrocarbon, viz., tetramethyl-methane.

Silicic Tetrethide, $Si(C_2H_5)_4$, prepared like the methyl-compound, is a liquid boiling at 153°. With chlorine it yields the monochlorinated derivative, $Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4Cl\end{matrix}\right.$, which boils at 185°, and reacts exactly like the chloride of a hydrocarbon, being converted by potassium acetate into the acetic ether, $Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4(OC_2H_3O)\end{matrix}\right.$, which boils at 211°, and is decomposed by alkalis into acetic acid, and an alcohol having the composition $Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4.OH\end{matrix}\right.$. This alcohol is a liquid insoluble in water, and boiling at 190°.

Silicic tetrethide and its derivatives may be regarded as *nonyl-compounds* in which 1 atom of carbon is replaced by silicon ; thus :

$Si(C_2H_5)_4 = SiC_8H_{20}$ . . . . . Silicononane,

$Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4Cl\end{matrix}\right. = SiC_8H_{19}Cl$ . . . . Siliconony1 chloride,

$Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4.O.C_2H_3O\end{matrix}\right. = SiC_8H_{19}(O.C_2H_3O)$ „ acetate,

$Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4(OH)\end{matrix}\right. = SiC_8H_{19}(OH)$ „ alcohol.

Ethylated Silicic Ethers.—When normal silicic ether, $Si(OC_2H_5)_4$, is heated with zinc-ethyl and sodium, one or all of the ethoxyl-groups are replaced by ethyl, the product being a mixture of mono-, di-, and triethylated silicic ethers, and silicic tetrethide, which may be separated by fractional distillation.

Triethylsilicic ether, $(C_2H_5)_3Si.(OC_2H_5)$, or *Silicoheptyl-ethyl oxide,* $SiC_6H_{15}.O.C_2H_5$, is a liquid, of specific gravity 0·841 at 0°, boiling at 153°, insoluble in water. Treated with acetic anhydride, it yields an acetic ether, convertible by the action of potash into triethyl silicon-hydroxide, $(C_2H_5)_3Si(OH)$, which is a tertiary silicic alcohol, analogous to triethyl-carbinol, and is hence called triethyl-silicol. It is a colourless, oily liquid, smelling like camphor, insoluble in water, boiling at 154°.

Diethylsilicic ether, $(C_2H_5)_2Si(OC_2H_5)_2$, is a fragrant liquid, insoluble in water, boiling at 155·8°, and having a specific gravity of 0·875 at 0°. When heated with acetyl chloride, it yields the compounds $(C_2H_5)_2Si(OC_2H_5)Cl$ and $(C_2H_5)_2SiCl_2$. The latter is a fuming liquid, boiling at 148°, and converted by water into diethylsilicic oxide $(C_2H_5)_2SiO$, analogous to diethyl ketone, $(C_2H_5)_2CO$.

Monethyl silicic ether, $(C_2H_5)Si(OC_2H_5)_3$, is a liquid smelling like camphor, boiling at 159°, slowly decomposed by water. Heated with acetyl chloride, it yields ethylsilicon trichloride,

$(C_2H_5)SiCl_3$, a strongly fuming liquid which boils at 100°, and is converted by water into ethylsilicic or silicopropionic acid, $C_2H_5.SiO.OH$. This acid is a white amorphous powder, which smoulders away when heated in the air, and dissolves in aqueous potash and soda forming silico-propionates.

ORGANO-METALLIC COMPOUNDS.

The name is especially applied to compounds of alcohol-radicles with metals not belonging to the pentad group. Those containing the more basic metals, such as zinc, are formed by the direct action of the metals, or better, of their sodium alloys, on the alcoholic iodides: *e.g.*,

$$\underset{\text{Zinc-sodium.}}{ZnNa_2} + 2C_2H_5I = 2NaI + \underset{\text{Zinc ethide.}}{Zn(C_2H_5)_2}$$

Those containing the less basic metals (tin, lead, &c.) are produced by the action of organo-zinc or mercury-compounds on metallic chlorides; *e.g.*,

$$SnCl_4 + 2Zn(C_2H_5)_2 = 2ZnCl_2 + Sn(C_2H_5)_4.$$

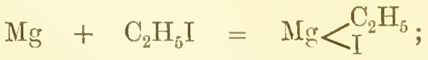
Potassium Ethide, C_2H_5K, and **Sodium Ethide**, C_2H_5Na, are known only in combination or mixture with zinc ethide, in which state they are obtained by the action of potassium or sodium on zinc ethide. These compounds and their homologues, discovered by Wanklyn, have played an important part in chemical synthesis. They absorb carbon-dioxide, producing salts of the fatty acids:

$$C_2H_5Na + CO_2 = \underset{\text{Sodium propionate.}}{C_2H_5.CO_2Na}.$$

By the action of *carbon monoxide* they are converted into ketones:

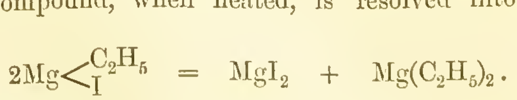
$$2C_2H_5Na + CO = Na_2 + (C_2H_5)_2CO.$$

Magnesium Ethide, $Mg(C_2H_5)_2$.—When ethyl iodide is heated with magnesium filings in a vessel from which the air is excluded, magnesium ethiodide is formed in the first instance according to the equation:



$$Mg + C_2H_5I = Mg{<}^{C_2H_5}_{I};$$

and this compound, when heated, is resolved into iodide and ethide:



$$2Mg{<}^{C_2H_5}_{I} = MgI_2 + Mg(C_2H_5)_2.$$

Magnesium ethide is a liquid which takes fire spontaneously in the air, and is rapidly decomposed by water, with formation of ethane:

$$Mg(C_2H_5)_2 + H_2O = 2C_2H_6 + MgO.$$

Zinc Ethide or **Zinc-ethyl**, $Zn(C_2H_5)_2$, is formed by heating ethyl iodide with zinc in a sealed glass tube, or for larger quantities, in a strong and well-closed copper cylinder. The reaction takes place in the same manner as with magnesium, zinc ethiodide, $Zn(C_2H_5)I$, being formed in the first instance as a white crystalline mass, which when distilled in an atmosphere of hydrogen, is resolved into zinc-iodide and zinc-ethide, the latter distilling over.

Zinc-ethide is is a mobile and very volatile disagreeable-smelling liquid, having a specific gravity of 1·182, and boiling at 118°. It takes fire instantly on coming in contact with the air, diffusing white fumes of zinc oxide. *Water* decomposes it violently, with formation of zinc hydroxide, and evolution of ethane:

$$Zn(C_2H_5)_2 + 2H_2O = ZnH_2O_2 + 2C_2H_6.$$

When gradually mixed with dry *oxygen*, it passes through two stages of oxidation, yielding first zinc-ethyl-ethoxide, $Zn\left\{\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}\right.$, and finally zinc-ethoxide, $Zn(OC_2H_5)_2$. With *iodine* and other halogens, the reaction also takes place by two stages, but consists in the successive substitution of the halogen for the ethyl; thus:

$$Zn(C_2H_5)_2 + I_2 = C_2H_5I + Zn(C_2H_5)I,$$

and

$$Zn(C_2H_5)I + I_2 = C_2H_5I + ZnI_2.$$

Zinc Methide, $Zn(CH_3)_2$, prepared in like manner, is a mobile spontaneously inflammable liquid, which boils at 46°, and resembles the ethyl compound in all its reactions.

Zinc Isopropide, $Zn(C_3H_7)_2$, boils at 146°. **Zinc isopentide**, or **Zinc amylide**, $Zn(C_5H_{11})_2$, boils at 220°, and fumes strongly in the air, but does not take fire spontaneously.

These organo-zinc compounds, discovered by Frankland, are very important reagents in organic synthesis, serving to effect the substitution of the positive radicle ethyl, &c., for chlorine, iodine, and other negative elements, and thus enabling us to build up carbon-compounds from others lower in the scale. With *carbon oxychloride* (phosgene) they form ketones:

$$COCl_2 + Zn(CH_3)_2 = ZnCl_2 + \underset{\text{Acetone.}}{CO(CH_3)_2};$$

also with the *chlorides* of *acid radicles* at ordinary temperatures: *e.g.*,

$$2(CH_3.COCl) + Zn(C_2H_5)_2 = ZnCl_2 + \underset{\text{Methyl-ethyl ketone.}}{2CO<\begin{matrix}CH_3\\C_2H_5\end{matrix}}$$

They also serve, as already mentioned, for the preparation of other organo-metallic bodies; *e.g.*,

$$Zn(C_2H_5)_2 + HgCl_2 = ZnCl_2 + Hg(C_2H_5)_2$$
$$2Zn(C_2H_5)_2 + SnCl_4 = 2ZnCl_2 + Sn(C_2H_5)_4$$
$$3Zn(C_2H_5)_2 + 2AsCl_3 = 3ZnCl_2 + 2As(C_2H_5)_3.$$

Sulphur dioxide is absorbed by these zinc-compounds, with formation of the zinc salts of methyl- and ethyl-dithionic or sulphinic acids (p. 114). *Nitrogen dioxide* dissolves in zinc-ethide, forming a crystalline compound, which, by the action of water and carbon dioxide, is converted into the zinc salt of dinitroethylic acid, $C_2H_5.N_2O_2H$, the structure of which has not yet been satisfactorily made out.

Mercuric Ethide, $Hg(C_2H_5)_2$.—This compound is formed by the action of mercuric chloride on zinc ethide, but it is more easily prepared by the action of sodium-amalgam on ethyl iodide in presence of acetic ether:

$$2C_2H_5I + Na_2 + Hg = 2NaI + Hg(C_2H_5)_2 .$$

The acetic ether takes no part in the reaction; nevertheless its presence appears to be essential.

Mercuric ethide is a transparent colourless liquid, boiling at 159°, and having a sp. gr. of 2·44. It burns with a smoky flame, giving off a large quantity of mercurial vapour. Chlorine, bromine, and iodine remove one equivalent of ethyl from this compound, and take its place, forming mercuric chlorethide, &c.; thus:

$$Hg(C_2H_5)_2 + Cl_2 = C_2H_5Cl + Hg(C_2H_5)Cl .$$

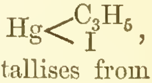
A similar action is exerted by acids, *e.g.*, by hydrobromic acid, the products being ethane and mercuric bromethide:

$$Hg(C_2H_5)_2 + HBr = C_2H_6 + Hg(C_2H)_5Br .$$

The chlorethide or bromethide is converted by water into mercuric ethyl-hydrate, $Hg(C_2H_5)(OH)$. Mercuric ethide serves for the preparation of several other organo-metallic bodies.

Mercuric Methide, $Hg(CH_3)_2$, prepared by similar processes, is a liquid slightly soluble in water, boiling at 95°, and having a specific gravity of 3·069.

Mercuric Isopentide or **Amylide,** $Hg(C_5H_{11})_2$, is a thick liquid, of specific gravity 1·66, decomposed by distillation.

Mercuric Allyliodide,  $Hg\!<\!{}^{C_3H_5}_{I}$, produced by agitating allyl iodide with mercury, crystallises from alcohol in silvery laminæ, melting at 135°. With hydrogen iodide, it yields mercuric iodide and propene:

$$Hg(C_3H_5)I + HI = HgI_2 + C_3H_6 ,$$

Aluminium Methide, $Al(CH_3)_3$, or $Al_2(CH_3)_6$.—This compound, discovered by Buckton and Odling, is formed by heating mercuric methide with aluminium. It is a mobile liquid, which crystallises at a little above 0°, and boils at 130°. At and above 220° the density of its vapour, compared with that of air, is 2·8, which is near to the theoretical density calculated for the formula $Al(CH_3)_3$, namely, 2·5. This seems to show that the true formula of the compound is $Al(CH_3)_3$, and not $Al_2(CH_3)_6$, and, consequently, that aluminium is a triad, not a tetrad (i. 265). At temperatures near the boiling point, however, the vapour-density becomes 4·4, approximating to the theoretical destiny calculated for the formula, $Al_2(CH_3)_6$.

Aluminium Ethide, $Al(C_2H_5)_2$, or $Al_2)(C_2H_5)_6$, resembles the methyl compound. It boils at 194°, and its vapour likewise exhibits, at temperatures considerably above its boiling point, a density nearly equal to that required by the formula $(Al(C_2H_5)_3$, for a two-volume condensation.

Tin Compounds.—Tin forms two ethyl-compounds, $Sn(C_2H_5)_2$ and $Sn(C_2H_5)_4$, analogous to stannous and stannic chloride; also a stannoso-stannic ethide, $Sn_2(C_2H_5)_6$, analogous in constitution to ethane, C_2H_6. Stannic ethide is a saturated compound, but the other two are unsaturated bodies, capable of uniting with chlorine, bromine, oxygen, and acid radicles, and being thereby converted into compounds of the stannic type.

STANNOUS ETHIDE, $Sn(C_2H_5)_2$.—When ethyl iodide and tinfoil are heated together in a sealed glass tube to about 150° or 180°, stannic iodethide, $Sn(C_2H_5)_2I_2$, is produced, crystallising in colourless needles. The same compound is obtained when tin and ethyl iodide are exposed to the rays of the sun concentrated by a concave mirror. The reaction is considerably facilitated if the tin be alloyed with one-tenth of its weight of sodium. This iodide is decomposed by sodium or zinc, which abstracts the iodine, and leaves stannous ethide in the form of a thick, oily liquid, insoluble in water, having the sp.gr. 1·558, and decomposed by distillation. Stannous ethide combines directly with 2 atoms of chlorine, iodine, and bromine, forming stannic chlorethide, $Sn^{iv}(C_2H_5)_2Cl_2$, &c. Exposed to the air, it absorbs oxygen, and is converted into stannic oxethide, $Sn^{iv}(C_2H_5)_2O$, a whitish, tasteless, inodorous powder, which when treated with oxygen acids, yields well crystallised stannic salts, such as $Sn(C_2H_5)_2(NO_3)_2$, $Sn(C_2H_5)_2SO_4$, &c.

STANNOSO-STANNIC ETHIDE, $Sn_2(C_2H_5)_6$, is always produced in small quantity when stannous ethide is prepared by the methods above mentioned. It is readily obtained in the free state by digesting an alloy of 1 part of sodium and 5 parts of tin with ethyl iodide, exhausting the mass with ether, evaporating the ethereal solution, and exhausting the residue with alcohol. The stannoso-stannic ethide, being insoluble in that liquid, then remains behind. It is a yellow oil, boiling at 180°, combining directly with chlorine, bromine, and iodine to form two molecules of a stannic compound; *e.g.*,

$$Sn_2(C_2H_5)_6 \quad + \quad Cl_2 \quad = \quad 2Sn^{iv}(C_2H_5)_3Cl\ ;$$

Stannic chloro-triethide.

also with oxygen, forming distannic oxy-hexethide, $Sn^{iv}_2(C_2H_5)_6O$. This oxide is, however, best obtained by distilling stannic oxydiethide, $Sn^{iv}(C_2H_5)_2O$ (above described), with potash. It is an oily liquid, soluble in alcohol, ether, and water; the aqueous solution has a strong alkaline reaction. It is easily acted upon by oxygen-acids, yielding the corresponding sulphate, $Sn_2(C_2H_5)_6SO_4$, &c.

STANNIC ETHIDE, $Sn^{iv}(C_2H_5)_4$, is produced by the action of zinc ethide on stannic chloride; also by the distillation of stannous ethide: $2Sn(C_2H_5)_2 = Sn + Sn(C_2H_5)_4$. It is a colourless, nearly odourless liquid, of sp. gr. 1·19, boiling at 181°, and very inflammable, burning with a highly luminous flame. When treated with chlorine, bromine, &c., or with acids, it forms substitution-products: thus, with iodine, it splits up into ethyl iodide and stannic iodotriethide:

$$Sn(C_2H_5)_4 + I_2 = C_2H_5I + Sn(C_2H_5)_3I,$$

with strong hydrochloric acid, it yields ethane and stannic chlorotriethide, $Sn(C_2H_5)_4 + HCl = C_2H_6 + Sn(C_2H_5)_3Cl$.

Stannous Methide, $Sn(CH_3)_2$, and Stannic Methide, $Sn(CH_3)_4$, resemble the corresponding ethyl compounds, and are obtained by similar reactions.

Plumbic Ethide, $Pb(C_2H_5)_4$, is produced by the action of plumbic chloride on zinc ethide:

$$2Zn(C_2H_5)_2 + 2PbCl_2 = 2ZnCl_2 + Pb + Pb(C_2H_5)_4.$$

It is a colourless limpid liquid, soluble in ether but not in water. When protected from the air, it boils, with partial decomposition, at about 200°. It is not acted upon by oxygen at ordinary temperatures, but chlorine, bromine, and iodine act violently upon it, in the same manner as on stannic ethide, forming plumbic chloro-triethide, $Pb(C_2H_5)_3Cl$, &c. Plumbic ethide is interesting, as affording a proof that lead is really a tetrad (p. 308).

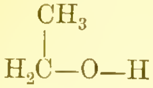
ALDEHYDES.

THESE are bodies containing the bivalent group CO, associated, on the one hand, with a monatomic alcohol radicle, and on the other with hydrogen; *e.g.*,

$$H—CO—CH_3 \qquad\qquad H—CO—C_4H_9$$

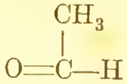
Acetic aldehyde. Valeric aldehyde.

They are derived from primary alcohols by elimination of one or more molecules of hydrogen (H_2), without introduction of an equivalent quantity of oxygen, so that they hold a position intermediate between the alcohols and the acids; thus:



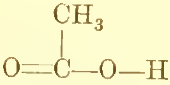
$$\begin{array}{l} \quad CH_3 \\ \quad | \\ H_2C-O-H \end{array}$$

Ethyl alcohol.



$$\begin{array}{l} \quad\ \ CH_3 \\ \quad\ \ | \\ O{=}C-H \end{array}$$

Acetic aldehyde.



$$\begin{array}{l} \quad\ \ CH_3 \\ \quad\ \ | \\ O{=}C-O-H \end{array}$$

Acetic acid.

The hydrogen eliminated in the conversion of a primary alcohol into an aldehyde is that which belongs to the group CH_2OH; consequently a monatomic alcohol can yield but one aldehyde; but a diatomic alcohol can yield two, by removal of H_2 and of $2H_2$; a triatomic alcohol three, and so on. At present, however, we are acquainted only with aldehydes derived from monatomic and diatomic alcohols.

Aldehydes derived from Monatomic Alcohols.

Of these aldehydes there are two series belonging to the fatty group, viz.:

1. *Aldehydes*, $C_nH_{2n}O$, *corresponding with the Fatty acids.*

Formic aldehyde, . .	CH_2O	Caproic aldehyde,. .	$C_6H_{12}O$
Acetic aldehyde, . .	C_2H_4O	Œnanthylic aldehyde,	$C_7H_{14}O$
Propionic aldehyde, .	C_3H_6O	Caprylic aldehyde, .	$C_8H_{16}O$
Butyric aldehyde, . .	C_4H_8O	Euodic aldehyde, .	$C_{11}H_{22}O$.
Valeric aldehyde, . .	$C_5H_{10}O$		

2. *Aldehydes*, $C_nH_{2n-2}O$, *corresponding with the Acrylic acids.*

Acrylic aldehyde, or Acrolein, . .	C_3H_4O
Crotonic aldehyde, ...	C_4H_6O.

All these aldehydes contain two atoms of hydrogen less than the corresponding alcohols, and one atom of oxygen less than the corresponding acids.

The aldehydes of the fatty groups are produced:—1. By oxidation of primary alcohols, either by the action of atmospheric oxygen, or by that of a mixture of dilute sulphuric acid and potassium dichromate or manganese dioxide, or by the action of chlorine on the alcohol diluted with water, the chlorine in this case decomposing the water, and thus acting as an oxidising agent; *e.g.*,

$$\begin{array}{l} CH_3 \\ | \\ CH_2OH \end{array} + O = H_2O + \begin{array}{l} CH_3 \\ | \\ COH \end{array}$$

Ethyl alcohol. Acetic aldehyde.

2. By distilling an intimate mixture of the calcium salt of the corresponding acid with calcium formate; *e.g.*,

$$\underset{\text{Acetic Acid.}}{CH_3.CO.OH} + \underset{\text{Formic acid.}}{H.CO.OH} = CO_2 + H_2O + \underset{\text{Acetic aldehyde.}}{CH_3.CO.H}$$

3. By the action of nascent hydrogen on the anhydrides and chlorides (chloranhydrides) of the fatty acids:

$$CH_3.COCl + H_2 = HCl + CH_3.COH$$

Acetyl chloride. — Acetic aldehyde.

$$\left.\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\right>O + 2H_2 = H_2O + 2(CH_3.COH).$$

Acetic Anhydride.

4. From the corresponding di-halogen derivatives of the hydrocarbons, by heating with water, or better, with lead oxide:

$$CH_3.CHCl_2 + PbO = PbCl_2 + CH_3.CHO.$$

Ethidene chloride.

5. By the slow oxidation of albuminous substances by means of manganese dioxide and sulphuric acid.

Some of the aldehydes occur in the essential oils of plants.

The aldehydes are colourless, neutral, volatile liquids, having more or less pungent odours. Only the lower aldehydes are soluble in water.

Reactions.—1. Aldehydes are easily converted by *oxidation* into the corresponding acids, either on exposure to the air or by contact with moist silver oxide, in the latter case with reduction of metallic silver:

$$CH_3.COH + 3AgOH = CH_3.CO.OAg + 2H_2O + Ag_2.$$

Acetic aldehyde. — Silver acetate.

This oxidation takes place with peculiar facility with ammoniacal silver solution, the silver being frequently deposited in a bright specular film.

2. Aldehydes fused with *potash* are converted into the corresponding acids, with evolution of hydrogen; *e.g.*,

$$C_5H_{10}O + KOH = C_5H_9KO_2 + H_2.$$

Valeric aldehyde. — Valeric acid.

3. *Nascent hydrogen*, evolved by the action of water on sodium amalgam, converts them into the corresponding alcohols; *e.g.*, $C_2H_4O + H_2 = C_2H_6O$. If, however, the aldehyde belongs to a non-saturated series, the action goes further, an additional quantity of hydrogen being then taken up, whereby the alcohol first formed is converted into a saturated alcohol belonging to another series; thus:

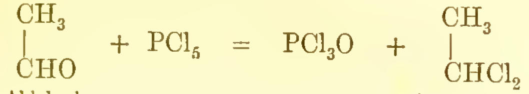
$$C_3H_4O + H_2 = C_3H_6O \text{ ; and } C_3H_6O + H_2 = C_3H_8O.$$

Acrylic aldehyde. — Allyl alcohol. — Allyl alcohol. — Propyl alchohol.

Nascent hydrogen evolved by the action of zinc on sulphuric acid does not appear to unite with aldehydes.

4. *Phosphorus pentachloride* converts aldehydes into chloralde-

hydes, compounds derived from aldehydes by substitution of Cl_2 for O; thus:



$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} + PCl_5 = PCl_3O + \begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix}$$

Aldehyde. Chloraldehyde.

The compounds thus produced are isomeric with the chlorides of the olefines; *e.g.*, acetic chloraldehyde, $CH_3.CHCl_2$, or ethidene chloride, with ethene chloride, $C_2H_4.Cl_2$ (p. 69).

5. *Chlorine* and *bromine* convert aldehydes into chlorides and bromides of acid radicles:

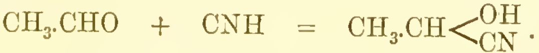
$$\underset{\text{Aldehyde.}}{C_2H_4O} + Cl_2 = HCl + \underset{\text{Acetyl chloride.}}{C_2H_3O.Cl}$$

$$\underset{\text{Aldehyde.}}{C_2H_4O} + 2Cl_2 = 2HCl + \underset{\text{Chloracetyl chloride.}}{C_2H_2ClO.Cl}$$

6. The *alkali-metals* dissolve in aldehydes, eliminating an equivalent quantity of hydrogen:

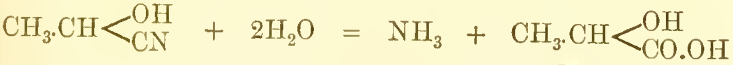
$$2C_2H_4O + K_2 = H_2 + 2C_2H_3KO.$$

7. Aldehydes heated with *hydrocyanic* and *hydrochloric acid* are converted, first into cyanhydrins, which then, by the action of the hydrochloric acid, or by that of alkalis, are converted into oxy-acids; thus:



$$CH_3.CHO + CNH = CH_3.CH{<}\begin{matrix} OH \\ CN \end{matrix}.$$

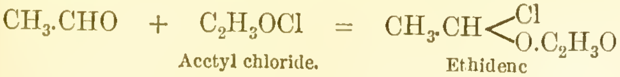
Aldehyde. Ethidene-cyanhydrin.



$$CH_3.CH{<}\begin{matrix} OH \\ CN \end{matrix} + 2H_2O = NH_3 + CH_3.CH{<}\begin{matrix} OH \\ CO.OH \end{matrix}$$

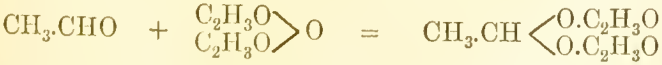
Lactic acid.

8. Aldehyde likewise unites with other carbon-compounds, as with the anhydrides and chlorides of the fatty acids, forming compound ethers:



$$CH_3.CHO + C_2H_3OCl = CH_3.CH{<}\begin{matrix} Cl \\ O.C_2H_3O \end{matrix}$$

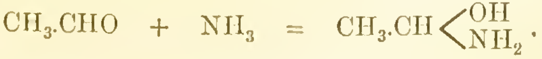
Acetyl chloride. Ethidene chloro-acetate.



$$CH_3.CHO + \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}{>}O = CH_3.CH{<}\begin{matrix} O.C_2H_3O \\ O.C_2H_3O \end{matrix}$$

Acetic anhydride. Ethidene diacetate.

9. Aldehydes combine with ammonia, forming compounds called aldehyde-ammonias, the mode of formation of which is shown in the following equation:



$$CH_3.CHO + NH_3 = CH_3.CH{<}\begin{matrix} OH \\ NH_2 \end{matrix}.$$

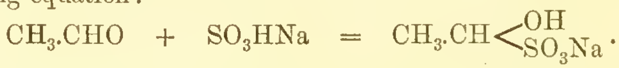
These compounds are easily soluble in water, but insoluble in ether, and are therefore precipitated by ammonia from the ethereal solutions of the aldehydes. They are rather unstable, and are easily resolved by acids into ammonia and the aldehydes.

10. Aldehydes also unite with *aniline*, water being eliminated, and form bases derived from a double molecule of aniline, $(C_6H_7N)_2$, by substitution of two equivalents of a diatomic radicle for four atoms of hydrogen; *e.g.*,

$$2C_2H_4O + 2C_6H_7N = 2H_2O + C_{12}H_{10}(C_2H_4)_2N_2$$

Acetic aldehyde. Aniline. Diethidene-dianiline.

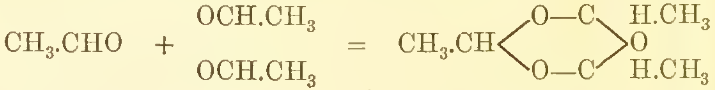
11. All aldehydes unite directly with the *acid sulphites of the alkali-metals*, forming crystalline compounds, which may be regarded as salts of ethidene-oxysulphonic acid (p. 175), as shown by the following equation:



$$CH_3.CHO + SO_3HNa = CH_3.CH{<}\begin{matrix}OH\\ SO_3Na\end{matrix}.$$

From these salts, the aldehydes may be separated by distillation with dilute sulphuric acid or solution of sodium carbonate. The reaction affords a ready means of purifying the aldehydes, and of detecting their presence in mixtures.

12. Under the influence of certain reagents (small quantities of acids, alkalis, and salts) two or more molecules of an aldehyde may unite together, forming a polymeride; *e.g.*,



$$CH_3.CHO + \begin{matrix}OCH.CH_3\\ \\ OCH.CH_3\end{matrix} = CH_3.CH{<}\begin{matrix}O—CH.CH_3\\ \qquad {>}O\\ O—CH.CH_3\end{matrix}$$

Aldehyde (3 mol). Paraldehyde.

ALDEHYDES BELONGING TO THE SERIES $C_nH_{2n}O$.

Formic Aldehyde, CH_2O or H.CHO, also called *Methylic aldehyde.*—This compound, discovered by Hofmann, is produced when a current of air charged with vapour of methyl alcohol is directed upon an incandescent spiral of platinum wire; and by suitable condensing arrangements, a liquid may be obtained consisting of a solution of the aldehyde in methyl alcohol. This liquid, rendered slightly alkaline by ammonia, and gently warmed with silver nitrate, yields a beautiful specular deposit of silver, with greater ease even than ordinary acetic aldehyde. The same solution, heated with a few drops of caustic potash, deposits drops of a brownish oil, having the odour of the resin of acetic aldehyde.

Formic aldehyde is likewise obtained by the dry distillation of calcium formate: $Ca(CHO_2)_2 = CH_2O + CaCO_3$. It has not yet been obtained in the pure state; but on heating the distillate obtained as above, part of the formic aldehyde escapes, and another portion remains as a solid polymeric modification, viz.,

Paraformaldehyde or *Trioxymethene*, $C_3H_6O_3$ or $(CH_2)_3O_3$, a compound likewise formed by the action of oxide or oxalate of silver on methene iodide, CH_2I_2, or best by distilling glycollic acid with a small quantity of sulphuric acid. It is a crystalline mass, insoluble in water, alcohol, and ether, melting at 152°, subliming below 100°. Its vapour-density, 1·06, corresponds with the formula CH_2O, showing that the molecule $C_3H_6O_3$ is split up when heated, into three molecules of formaldehyde. On cooling, however, the triple molecule is reproduced. $C_3H_6O_3$ is also converted into CH_2O when heated with water to 130°.

When ammonia is passed over paraformaldehyde, hexmethenamine, $C_6H_{12}N_4 = (CH_2)_6N_4$, is produced, a base which crystallises from alcohol in shining rhombohedrons, and sublimes without alteration when cautiously heated. It is a monoacid base, forming crystalline salts, the hydrochloride, $C_6H_{12}N_4$, HCl, for example. By boiling with dilute acids it is reconverted into formaldehyde.

Parathioformaldehyde or *Trithiomethene*, $(CH_2)_3S_3$, is produced by passing hydrogen sulphide into the aqueous solution of formaldehyde, also by the action of zinc and hydrochloric acid on carbon bisulphide, and by heating methene iodide with potassium sulphide in alcoholic solution. It is a solid body having an alliaceous odour, is insoluble in water, but dissolves in alcohol, and crystallises therefrom in slender needles, melting at 218°, and easily subliming. The vapour-density agrees with the formula $C_3H_6S_3$, whence it is inferred that solid paraformaldehyde is correctly represented by the formula $C_3H_6O_3$. The thioaldehyde, $C_3H_6S_3$, heated to 170° with silver sulphate, is converted into $C_3H_6O_3$.

Acetic Aldehyde, or **Acetaldehyde**, $C_2H_4O = CH_3.CHO = C_2H_3O.H$, also called *Ethyl Aldehyde*, but more generally by the simple name aldehyde.*—This substance is formed by oxidation of ethyl-alcohol; also among other products, when the vapour of ether or alcohol is transmitted through a red-hot tube; by the action of chlorine on weak alcohol; and by the other general reactions above-mentioned. It is best prepared by the following process: 6 parts of oil of vitriol are mixed with 4 parts of rectified spirit of wine, and 4 parts of water; this mixture is poured upon 6 parts of powdered manganese dioxide contained in a capacious retort, in connection with a condenser cooled by ice-cold water; gentle heat is applied, and the process is interrupted when 6 parts of liquid have passed over. The distilled product is put into a small retort, with its own weight of calcium chloride, and redistilled; and this operation is repeated. The aldehyde, still retaining alcohol and other impurities, is mixed with twice its volume of ether, and saturated with dry ammoniacal gas; a crystalline compound of aldehyde and ammonia then separates, which may be washed with a little ether, and dried in the air. From this substance the aldehyde may be separated by distillation in a water-bath with sulphuric acid diluted with an equal quantity of water; by careful rectification from calcium chloride, at a temperature not exceeding 30·5°, it is obtained pure and anhydrous.

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* Alcohol dehydrogenatum.

Considerable quantities of aldehyde occur in the "first runnings" obtained in the manufacture of alcohol from sugar-beet and from potatoes, being probably formed by oxidation of the spirit during the filtration through charcoal, to which it is subjected for the removal of fusel-oil and other impurities.

Aldehyde is a limpid, colourless liquid, of characteristic ethereal odour, which, when strong, is exceedingly suffocating. It has a density of 0·807 at 0°, boils at 21°–22°, and mixes in all proportions with water, alcohol, and ether: it is neutral to test-paper, but becomes acid on exposure to air, from production of acetic acid: under the influence of platinum-black this change is very speedy. When a solution of aldehyde is heated with caustic potash, a brown resin-like substance is produced, the so-called aldehyde-resin. It reduces silver oxide at a gentle heat, without evolution of gas, the metal being deposited on the inner surface of the vessel as a brilliant and uniform film; the liquid contains silver acetate.

The principal reactions of aldehyde have been already mentioned (p. 246). It is converted by nascent hydrogen into ethyl alcohol, by oxidation into acetic acid; by phosphorus pentachloride into chloraldehyde or ethidene dichloride, $CH_3—CHCl_2$. It unites with the acid sulphites of the alkali-metals, forming compounds like the ammonium salt, $CH_3.CH{<}\begin{smallmatrix}OH\\O.SO_3(NH_4)\end{smallmatrix}$, which are resolved at 100° into aldehyde, sulphurous oxide, and neutral sulphites; thus:

$$2[CH_3.CH{<}\begin{smallmatrix}OH\\SO_3K\end{smallmatrix}] = 2(CH_3.CHO) + SO_3K_2 + SO_2 + H_2O.$$

Aldehyde unites also with *acetic oxide*, forming the compound $C_2H_4O.(C_2H_3O)_2O$ or $CH_3.CH{<}\begin{smallmatrix}OC_2H_3O\\OC_2H_3O\end{smallmatrix}$, and with *ethyl oxide*, forming ethidene diethylate or acetal, $CH_3.CH{<}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$; in like manner with *methyl oxide*, forming ethidene dimethylate, $CH_3.CH(OCH_3)_2$, (p. 174).

With dry *hydrogen cyanide*, aldehyde forms the compound $CH_3.CH{<}\begin{smallmatrix}OH\\CN\end{smallmatrix}$, a liquid soluble in water and in alcohol, boiling at 183°, with partial decomposition into aldehyde and hydrogen cyanide, and converted, by heating with strong hydrochloric acid or with alkalis, into α-lactic acid, $CH_3.CH{<}\begin{smallmatrix}OH\\CO_2H\end{smallmatrix}$.

Aldehyde-ammonia, $C_2H_4O.NH_3 = CH_3.CH{<}\begin{smallmatrix}OH\\NH_2\end{smallmatrix}$, obtained by passing dry ammonia gas into an ethereal solution of aldehyde, crystallises in large shining rhombohedrons; it has a mixed odour of ammonia and turpentine, dissolves very easily in water, with less facility in alcohol, and with difficulty in ether; melts at about 76°, and distils unchanged at 100°. Acids decompose it, with production of ammoniacal salts and separation of aldehyde. Hydrogen sulphide converts it into thialdine, $C_6H_{13}NS_2$. Sulphurous oxide gas is rapidly absorbed by a solution of aldehyde-ammonia, forming the crystalline compound $C_2H_4O.NH_3.SO_2$, isomeric with taurine (p. 174), and with the compound formed by direct combination of aldehyde with acid ammonium sulphite.

Polmeric Modifications of Aldehyde.—Pure anhydrous aldehyde, treated at ordinary temperatures with a small quantity of gaseous hydrochloric acid, sulphurous oxide, or carbonyl chloride (phosgene), or of zinc chloride or strong sulphuric acid, is converted into a polymeride, called paraldehyde, which crystallises on cooling the liquid to 0°, in large transparent prisms, melting at 10·5° to a liquid which boils at 124°, has a specific gravity of 0·998 at 15°, and a vapour-density three times as great as that of aldehyde itself: hence its molecular formula is $C_6H_{12}O_3$. When distilled in contact with either of the reagents above mentioned, it is reconverted into ordinary aldehyde, but it does not undergo this change when heated alone.

When either of the same reagents acts on aldehyde cooled by a freezing mixture, another polymeric modification is formed, called metaldehyde, which also crystallises in transparent prisms or in white needles, but differs from paraldehyde in subliming when heated without previous fusion, and in being at the same time partly reconverted into aldehyde. In consequence of this transformation, its vapour-density, and therefore its molecular formula, have not been determined.

When aldehyde is left for some time in contact with dilute hydrochloric acid, two molecules of it unite in such a manner as to form the aldehyde of butene glycol, called aldol:

$$CH_3.CHO + CH_3.CHO = CH_3.CH(OH).CH_2.CHO.$$

Under the influence of certain other reagents, condensed products are formed by the union of two or more molecules of aldehyde, and elimination of the elements of water; thus when aldehyde is heated with zinc chloride, crotonic aldehyde is produced:

$$CH_3—CHO + CH_3—CHO = H_2O + CH_3—CH=CH—CHO.$$

Halogen Derivatives of Aldehyde.

Monochloraldehyde, $CH_2Cl.CHO$, formed by the action of sulphuric acid on chloracetal, $CH_2Cl—CH(OC_2H_5)_2$, is known only in aqueous solution. By exposure to the air, and by the action of silver oxide, it is converted into chloracetic acid.

Dichloraldehyde, $CHCl_2.CHO$, produced by distillation of dichloracetal with strong sulphuric acid, is a liquid insoluble in water, and boiling at 88°–90°. By keeping, it is gradually converted into two solid polymeric modifications, one of which is amorphous, and is reconverted into liquid dichloraldehyde at 120°, while the other crystallises from alcohol in large prisms, melts at 130°, and does not pass into the liquid modification till heated to 240°.

Trichloraldehyde or **Chloral,** $CCl_3.CHO$, is formed by the prolonged action of chlorine on ethyl alcohol. To prepare it, chlorine is passed into absolute alcohol as long as hydrochloric acid continues to be evolved, and the product is agitated with three times its volume of strong sulphuric acid. On gently warming the mixture in a water-bath, the impure chloral separates as an oily liquid, which floats on the surface of the acid; it is purified by distillation from fresh oil of vitriol, and afterwards from a small quantity of quicklime, which must be kept completely covered by the liquid until the end of the operation. Chloral has also been obtained from starch, by distillation with hydrochloric acid and manganese dioxide.

Chloral is a thin, oily, colourless liquid, of peculiar, pungent, tear-exciting odour: it has but little taste. When dropped upon paper it leaves a greasy stain, which is not, however, permanent. It has a density of 1·502, and boils at 94°, and changes on prolonged keeping into a solid polymeride. Chloral is freely soluble in water, alcohol, and ether; the aqueous solution is not affected by silver nitrate. Caustic baryta and lime decompose the vapour of chloral when heated in it, with appearance of ignition; the oxide is converted into chloride, carbon is deposited, and carbon monoxide is set free. Solutions of caustic alkalis also decompose it, with production of a formate and chloroform:

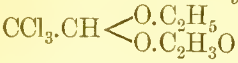
$$CCl_3.CHO + KOH = CHCl_3 + CHO.OK.$$

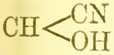
By oxidation with nitric acid, it is converted into trichloracetic acid.

With a small quantity of *water* chloral forms a hydrate, $C_2HCl_3O.H_2O = CCl_3.CH{<}^{OH}_{OH}$, which forms large monoclinic crystals, melting at 46°, and distilling at 96°–98°. It is easily soluble in water, has a peculiar odour, and sharp scratching taste, and produces sleep when taken internally or introduced under the skin. Strong sulphuric acid decomposes it into water and alcohol.

With *hydrogen sulphide*, chloral forms, in like manner, a crystalline sulphydrate, $CCl_3.CH{<}^{OH}_{SH}$, which melts at 77°, and boils at 123°.

With *alcohol*, chloral forms an alcoholate, $CCl_3.CH{<}^{OC_2H_5}_{OH}$ which is a crystalline body, melting at 56°, and boiling at 114°–115°

and decomposed by strong sulphuric acid, with reproduction of chloral. Treated with *acetyl chloride*, it is converted into the acetic ether,  $CCl_3.CH{<}^{O.C_2H_5}_{O.C_2H_3O}$, which boils at 198°.

Dibromaldehyde, $CHBr_2.CHO$, formed by direct bromination of aldehyde, is a liquid which boils at 140°–142°, is converted on standing into a solid polymeride, forms a crystalline hydrate, and unites with hydrogen cyanide, forming the compound, $CHBr_2.$  $CH{<}^{CN}_{OH}$, convertible into dibromolactic acid.

Tribromaldehyde or **Bromal,** $CBr_3.CHO$, formed by the action of bromine on alcohol, is a liquid very much like chloral, boiling at 172°–173°, and decomposed by alkalis into formic acid and bromoform. It forms a solid hydrate, melting at 53°, an alcoholate which melts at 44°, and decomposes at 100°, and with hydrogen cyanide the compound, $CBr_3.CH{<}^{CN}_{OH}$, convertible into tribromolactic acid.

Sulphur-derivatives of Aldehyde.—When hydrogen sulphide is passed through aqueous aldehyde, a compound of aldehyde and thioaldehyde is produced, in the form of an oil, having an offensive odour, solidifying at $-8°$, and converted by contact with hydrochloric acid into parathioaldehyde, $(C_2H_4S)_3$. This compound, analogous to paraldehyde, forms white needles, insoluble in water, and subliming at 45°. Its vapour-density agrees with the formula, $C_6H_{12}S_3$.

On passing hydrogen sulphide into an aqueous solution of aldehyde-ammonia, thialdine, $C_6H_{13}NS_2$, separates in large colourless crystals, melting at 43°, slightly soluble in water, easily in alcohol and ether, and having an offensive odour. It is a strong base; its hydrochloride has the composition $C_6H_{13}NS_2.HCl$.

On mixing an alcoholic solution of aldehyde-ammonia with *carbon bisulphide*, carbothialdine, $C_5H_{10}N_2S_2$, is formed in large shining crystals, separable by boiling with acids into aldehyde, carbon bisulphide, and ammonia.

Propionic Aldehyde, $C_3H_6O = CH_3.CH_2.CHO$, prepared by oxidation of normal propyl alcohol, or by distilling a mixture of calcium propionate and formate, is very much like acetaldehyde, has a specific gravity of 0·804 at 20°, boils at 49°, and dissolves in 5 volumes of water. With phosphorus pentachloride it forms propidene chloride, $CH_3.CH_2.CHCl_2$.

The higher aldehydes of the series are susceptible of isomeric modifications analogous to those of the primary alcohols. Only a few of those are however known: thus, of the four possible 5-carbon aldehydes, analogous to the four primary pentyl alcohols, two only have yet been obtained.

The following table exhibits the specific gravities and boiling points of these higher aldehydes. All of them are liquid at ordinary temperatures, except palmitic aldehyde, formed by oxidation of cetyl alcohol, which is a white crystalline mass:—

Aldehydes.			Boiling Point.	Spec. Gravity.
Butyric	Normal,	$CH_3.CH_2.CH_2.CHO$	75°	0·834 at 0°
	Iso,	$(CH_3)_2CH.CHO$	61°	0·822 at 0°
Valeric	Normal,	$CH_3.(CH_2)_3.CHO$	102°	
	Iso,	$(CH_3)_2CH.CH_2.CHO$	92°–93°	0·768 at 12°
Caproic (Iso,)		$(CH_3)_2CH.(CH_2)_2CHO$	121°	
Œnanthylic,		$CH_3.(CH_2)_5.CHO$	154°	0·827
Palmitic		$C_{16}H_{32}O$.	melts at 50°	

Isobutyric aldehyde treated with a small quantity of strong sulphuric acid, is converted into paraisobutyric aldehyde, $(C_4H_8O)_3$, which crystallises in shining needles, melting at 60°, and boiling at 194°.

Normal butyric aldehyde, heated with alcoholic ammonia to a temperature not exceeding 100°, yields two bases, dibutyraldine, $C_8H_{17}NO$, and tetrabutyraldine, $C_{16}H_{29}NO$, the former of which, when subjected to dry distillation, gives off H_2O, and is converted into paraconine, $C_8H_{15}N$, an oily base, very much like the conine of hemlock.

Trichlorobutyric aldehyde or *Butyric chloral*, $C_4H_5Cl_3O$, (formerly supposed to be crotonic chloral, $C_4H_3Cl_3O$), is formed, together with several other products, by the action of chlorine on acetaldehyde. It is a liquid boiling at 155°–165°.

Isovaleric aldehyde or *Valeral*, heated with alcoholic ammonia, yields two bases, valeridine, $C_{10}H_{19}N$, and valeritrine, $C_{15}H_{27}N$, the latter of which is a liquid, boiling at 250°–260°, and smelling like conine.

Œnanthylic Aldehyde or *Œnanthol*, is formed in the dry distillation of castor-oil. It oxidises in the air to œnanthylic acid, and is converted by nascent hydrogen into normal heptyl alcohol.

ALDEHYDES OF THE SERIES, $C_nH_{2n-2}O$.

These aldehydes are related to the alcohols of the allylic series in the same manner as the aldehydes, $C_nH_{2n}O$, are related to the fatty alcohols. They are unsaturated compounds, and capable of taking up 2 atoms of a monotomic element or radicle.

Acrylic Aldehyde or **Acrolein**, $C_3H_4O = CH_2{=}CH{-}CHO$, the lowest member of the series, is produced:

1. By the oxidation of allyl alcohol.
2. By the dehydration of glycerin, when that substance is heated with phosphoric oxide, strong sulphuric acid, or acid potassium sulphate: $C_3H_8O_3 - 2H_2O = C_3H_4O$.

It is always produced in the destructive distillation of neutral fats containing glycerin, and is the cause of the intolerably pungent odour attending that process.

Pure acrolein is a thin, colourless, highly volatile liquid, lighter than water, and boiling at 52·2°. Its vapour is intensly irritating. It is sparingly soluble in water, freely in alcohol and ether.

Acrolein, by keeping, undergoes partial decomposition, yielding a white, flocculent, indifferent body, disacryl; the same substance is sometimes produced, together with acrylic acid, by exposure to the air. In contact with *alkalis*, acrolein suffers violent decomposition, producing, like aldehyde, a resinous body. When exposed for some time to the air, or mixed with silver oxide, it is rapidly oxidised into acrylic acid, $C_3H_4O_2$.

Nascent hydrogen converts it into allyl alcohol. With *phosphorous pentachloride* it yields the compound $CH_2{=}CH{-}CHCl_2$, a liquid boiling at 84°. With *hydrochloric acid* acrolein forms a crystalline compound, $C_3H_4O.HCl$, which melts at 32°, and is resolved by distillation into hydrochloric acid and acrolein.

Acrolein mixed with alcoholic ammonia is immediately converted into acrolein-ammonia, C_6H_9NO:

$$2C_3H_4O + NH_3 = C_6H_9NO + H_2O.$$

This compound is a yellowish mass, which turns brown on drying. It forms amorphous salts, and yields picoline, C_6H_7N, by distillation.

Crotonic Aldehyde, $C_4H_6O = CH_3-CH{=}CH{-}CHO$, is produced by heating acetaldehyde to 100° with dilute hydrochloric acid, or with zinc chloride, and a little water:

$$CH_3.CHO + CH_3.CHO = H_2O + CH_3.CH{=}CH.CHO,$$

aldol being probably formed as an intermediate product.

Crotonic aldehyde is a colourless liquid, having an extremely pungent odour, and boiling at 104°–105°. In contact with the air, or with moist silver oxide, it is easily oxidised to crotonic acid. It unites with hydrogen chloride, forming monochlorobutyric aldehyde:

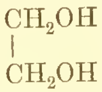
$$CH_3.CH{=}CH.CHO + HCl = CH_3.CH_2.CHCl.CHO.$$

Aldehydes derived from Diatomic Alcohols.

Diatomic alcohols can yield by oxidation two classes of aldehydes, according as one or two molecules of hydrogen (H_2) are removed. Propene glycol, $C_3H_8O_2$, for example, might yield the two aldehydes, $C_3H_6O_2$ and $C_3H_4O_2$. Only a few of these compounds have, however, been obtained.

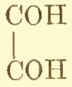
Of aldehydes derived from the glycols, $C_nH_{2n+2}O_2$, only three are at present known, viz., glyoxal, $C_2H_2O_2$, which is the second aldehyde of ordinary glycol, $C_2H_6O_2$; aldol, $C_4H_8O_2$, which is the first, and succinic aldehyde, $C_4H_6O_2$, which is the second aldehyde of butene glycol.

Glyoxal, $C_2H_2O_2$, and the aldehydic acid, glyoxylic acid, $C_2H_2O_3$, are intermediate in composition between glycol and oxalic acid:



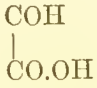
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol.



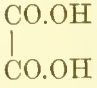
$$\begin{array}{l} COH \\ | \\ COH \end{array}$$

Glyoxal.



$$\begin{array}{l} COH \\ | \\ CO.OH \end{array}$$

Glyoxylic acid.



$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}$$

Oxalic acid.

Both are formed as intermediate products in the oxidation of glycol, and are converted by further oxidation into oxalic acid. They are, however, most easily obtained by oxidising ethyl alcohol with nitric acid.

Alcohol (2 parts) is introduced into a tall glass cylinder; 1 part of water is poured into the vessel through a funnel, the tube of which reaches to the bottom, and afterwards 1 part of fuming nitric acid is introduced in the same way, so as to form three distinct layers of liquid. The mixture is left to itself at a temperature of 20°–22° till the three liquids have become mixed; after which the mixture is evaporated in the water-bath, diluted with water, saturated with chalk at the boiling heat, then filtered, and the filtrate is mixed with alcohol, whereupon glycollate and glyoxylate of calcium are precipitated, and glyoxal remains in solution. On recrystallising the calcium salts, the glyoxylate crystallises out first, and afterwards the glycollate. The glyoxal is separated from the solution by agitation with acid sodium sulphite, with which it forms a crystalline compound; this sodium compound treated with barium chloride yields the corresponding barium compound; and from this the glyoxal may be separated by dilute suphuric acid.

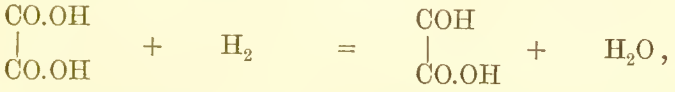
Glyoxal, $C_2H_2O_2 = \begin{array}{l} COH \\ | \\ COH \end{array}$, isomeric with glycollide, $\left.\begin{array}{l} CH_2 \\ | \\ CO \end{array}\right> O$, remains, on evaporating the solution obtained in the manner just described, as a transparent, amorphous, deliquescent mass, very soluble in water, alcohol, and ether. It reduces an ammoniacal solution of silver nitrate, forming a silver speculum. Nitric acid oxidises it to glycollic and oxalic acids. Being a double aldehyde (containing the group COH twice) it unites with two molecules of acid potassium sulphite, forming the compound $C_2H_2O_2(SO_3KH)_2$. When its solution in acetic acid is left in contact with a small quantity of hydrochloric acid, a condensation-product is formed, perhaps $C_{12}H_{12}O_{12}$.

Fixed caustic alkalis and alkaline earths convert glyoxal into salts of glycollic acid, *e.g.*, $C_2H_2O_2 + KOH = C_2H_3KO_3$. A syrupy solution of glyoxal heated with a strong solution of aqueous ammonia yields two crystalline bases, glyoxaline and glycosine:

$$\underset{\text{Glyoxal.}}{2C_2H_2O_2} + 2NH_3 = \underset{\text{Glyoxaline.}}{C_3H_4N_2} + \underset{\text{Formic acid.}}{CH_2O_2} + 2H_2O$$

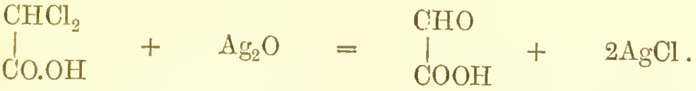
$$\underset{\text{Glyoxal.}}{3C_2H_2O_2} + 4NH_3 = \underset{\text{Glycosine.}}{C_6H_6N_4} + 6H_2O\,.$$

Glyoxylic or **Glyoxalic Acid,** $C_2H_2O_3 = CHO—CO_2H$, is formed by oxidation of alcohol as above described; also by reducing oxalic acid with zinc and hydrochloric acid:



$$\begin{array}{c} CO.OH \\ | \\ CO.OH \end{array} + H_2 = \begin{array}{c} COH \\ | \\ CO.OH \end{array} + H_2O\,,$$

and by heating dichloracetic acid with silver oxide, or ethylic dichloracetate with water to 120°:



$$\begin{array}{c} CHCl_2 \\ | \\ CO.OH \end{array} + Ag_2O = \begin{array}{c} CHO \\ | \\ COOH \end{array} + 2AgCl\,.$$

When concentrated, it forms a thick syrup easily soluble in water, and distils undecomposed with aqueous vapour.

The glyoxylates contain 1 molecule of water very closely combined, excepting the *ammonium salt*, which is anhydrous.

This salt, $C_2HO_3.NH_4$, crystallises in needles, and dissolves easily in water. The *silver salt*, $C_2HO_3Ag + H_2O$, is a white crystalline precipitate; the *calcium salt*, $(C_2HO_3)_2Ca + 2H_2O$, forms hard prisms, sparingly soluble in cold water.

Glyoxylic acid is readily oxidised to oxalic acid. By boiling its calcium salt with water, it is resolved into glycollic and oxalic acids:

$$2C_2H_2O_3 + H_2O = C_2H_4O_3 + C_2H_2O_4\,.$$

By nascent hydrogen (zinc and hydrochloric acid), it is converted into glycollic acid.

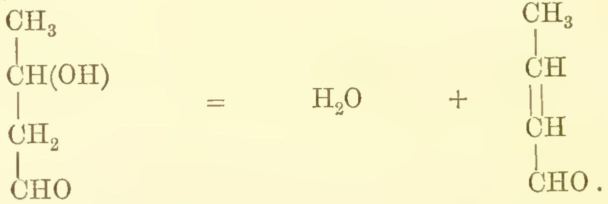
Glyoxylic acid is both acid and aldehyde. Its aldehydic nature is shown by its power of reducing an ammoniacal silver solution, and of forming double salts with alkaline bisulphites.

Aldol, $C_4H_8O_2$, the aldehyde of butene glycol, is polymeric with acetaldehyde, and is formed by combination of two molecules of that body, under the influence of dilute hydrochloric acid; thus:

$$CH_3.CHO + CH_3.CHO = CH_3.CH(OH).CH_2.CHO.$$

A cold mixture of acetaldehyde and dilute hydrochloric acid is left for two days till it acquires a yellow colour. The liquid is then neutralised with sodium carbonate, and shaken up with ether; the ether is evaporated; and the aldol which remains is evaporated in a vacuum.

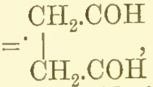
Aldol is a colourless inodorous liquid, of specific gravity 1·120 at 0°, not miscible with water. On standing it changes to a viscid liquid, which cannot be poured out of the containing vessel. In a vacuum it distils between 95° and 105°, but when heated under ordinary pressure it gives off water, and is converted into crotonic aldehyde:



$$\begin{array}{c}CH_3\\ |\\ CH(OH)\\ |\\ CH_2\\ |\\ CHO\end{array} = H_2O + \begin{array}{c}CH_3\\ |\\ CH\\ \|\\ CH\\ |\\ CHO\end{array}.$$

It reduces silver from the ammonio-nitrate, and when heated with water and silver oxide, is converted into β-oxybutyric acid:

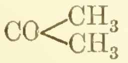
$$CH_3.CH(OH).CH_2.CO(OH).$$



Succinic Aldehyde, $C_4H_6O_2 = \begin{array}{l}CH_2.COH\\ |\\ CH_2.COH\end{array}$, is a liquid soluble in water, and boiling at 201°–203°. By oxidation it is converted into normal oxyisobutyric acid and succinic acid.

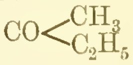
KETONES.

These bodies contain the group CO associated with two monatomic alcohol-radicles, which may either be the same or different, *e.g.*,



$$CO{<}\begin{array}{l}CH_3\\ CH_3\end{array}$$

Dimethyl ketone or Acetone.



$$CO{<}\begin{array}{l}CH_3\\ C_2H_5\end{array}$$

Methyl-ethyl ketone.

They may be regarded as derived from aldehydes by substitution of an alcohol-radicle for the hydrogen atom attached to the group CO; thus:

Acetic aldehyde,	$CH_3.CO.H$
Acetic ketone or acetone,	$CH_3.CO.CH_3$,

or as compounds of an alcohol-radicle with an acid radicle—acetone for example, as methyl-acetyl.

The only bodies of this class that have been carefully studied are those which contain the alcohol-radicles C_nH_{2n+1}, and are analogous to the aldehydes $C_nH_{2n}O$, and the fatty acids $C_nH_{2n}O_2$.

The ketones of this group, containing two equivalents of the same alcohol-radicle, are produced:

1. By the action of carbon monoxide on sodium ethide and its homologues:

$$CO \quad + \quad 2NaC_nH_{2n+1} \quad = \quad Na_2 \quad + \quad CO(C_nH_{2n+1})_2\,.$$

For example:

$$\underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{CO} \quad + \quad \underset{\text{Sodium-ethyl.}}{2NaC_2H_5} \quad = \quad Na_2 \quad + \quad \underset{\text{Propione.}}{CO(C_2H_5)_2}\,.$$

2. By the action of zinc-methyl and its homologues on the acid chlorides, $C_nH_{2n-1}OCl$; *e.g.*:

$$\underset{\text{Zinc methide.}}{Zn(CH_3)_2} \quad + \quad \underset{\substack{\text{Acetic}\\ \text{chloride.}}}{2COCH_3Cl} \quad = \quad ZnCl_2 \quad + \quad \underset{\text{Acetone.}}{2CO(CH_3)_2}$$

3. By the oxidation of the secondary alcohols; thus:

$$\underset{\text{Isopropyl alcohol.}}{CH(CH_3)_2.OH} \quad + \quad O \quad = \quad H_2O \quad + \quad \underset{\text{Acetone.}}{CO(CH_3)_2}\,.$$

4. By the dry distillation of the calcium-salts of the fatty acids; *e.g.*:

$$\underset{\text{Calcium acetate.}}{Ca\left\{\begin{matrix}O(COCH_3)\\ O(COCH_3)\end{matrix}\right.} \quad = \quad \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{COCaO_2} \quad + \quad \underset{\text{Acetone.}}{CO(CH_3)_2}$$

The ketones formed in this manner from the successive members of the fatty acid series differ from one another by twice CH_2; thus:

Acetic acid, . .	$C_2H_4O_2$,	yields	Acetone, . .	C_3H_6O .
Propionic acid, .	$C_3H_6O_2$,	„	Propione, .	$C_5H_{10}O$.
Butyric acid, .	$C_4H_8O_2$,	„	Butyrone, .	$C_7H_{14}O$.
Valeric acid, .	$C_5H_{10}O_2$,	„	Valerone, .	$C_9H_{18}O$.

The intervals are filled up by ketones containing different alcohol-radicles; thus ethyl-methyl ketone, C_4H_8O or $CO(CH_3)(C_2H_5)$, is intermediate between acetone and propione.

The ketones containing two different alcohol-radicles may be obtained by the second of the processes above given: *e.g.*:

$$\underset{\substack{\text{Acetic}\\ \text{chloride.}}}{2COCH_3Cl} \quad + \quad \underset{\text{Zinc ethyl.}}{Zn(C_2H_5)_2} \quad = \quad ZnCl_2 \quad + \quad \underset{\substack{\text{Ethyl-methyl}\\ \text{ketone.}}}{2CO(CH_3)(C_2H_5)}$$

Or by distilling a mixture of the calcium-salts of two different fatty acids; thus:

$$\underset{\text{Valerate.}}{Ca(CO_2C_4H_9)_2} + \underset{\text{Acetate.}}{Ca(CO_2CH_3)_2} = 2CaCO_3 + \underset{\text{Methyl-butyl ketone.}}{2CO(CH_3)(C_4H_9)}$$

The formation of aldehydes by distilling a mixture of a formate with the salt of another fatty acid (p. 245), is a particular case of this last reaction.

Ketones are also formed:—5. By the gradual oxidation of the acids of the lactic series, $C_nH_{2n}O_3$, with chromic acid mixture:

$$\underset{\text{Oxyisobutyric acid.}}{(CH_3)_2.C(OH).CO_2H} + O = CO_2 + H_2O + \underset{\text{Dimethyl ketone.}}{(CH_3)_2CO}.$$

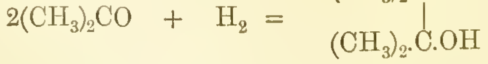
6. By the action of alkalis on the carbo-ketonic acids (*q.v.*).

7. By the dry distillation of wood, sugar, and many other carbon-compounds.

Every ketone is isomeric with an aldehyde belonging to the same series; thus acetone is isomeric with propionic aldehyde, $C_2H_5.COH$; butyrone, $CO(C_3H_7)_2$, with œnanthylic aldehyde, $C_6H_{13}.COH$, &c. Formic acetone, COH_2, is identical with formic aldehyde.

Ketones are, for the most part, volatile liquids, insoluble in water, and not capable of reducing an ammoniacal silver-solution. Those in which the group CO is associated with a methyl group, resemble the aldehydes in forming crystalline compounds with alkaline bisulphites, from which the ketone may be liberated by distillation with an alkali. Ketones differ from aldehydes: 1. In not being converted by oxidation into the corresponding acids.—2. In being converted by nascent hydrogen into secondary alcohols, whereas the aldehydes are converted into primary alcohols.—3. In not combining with aniline.

The formation of secondary alcohols by hydrogenation of ketones is attended, to a small amount, with a condensation of two ketone molecules, resulting in the formation of a diatomic alcohol (a pinacone); *e.g.*:

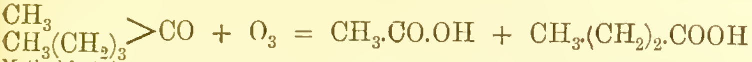


$$2(CH_3)_2CO + H_2 = \begin{array}{c}(CH_3)_2.C.OH \\ | \\ (CH_3)_2.C.OH\end{array}$$

Acetone. Pinacone.

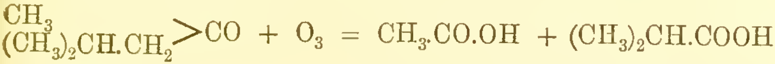
Ketones, like aldehydes, unite with *hydrogen cyanide*, forming cyanhydrins, acetone, for example, yielding $(CH_3)_2C{<}^{OH}_{CN}$, which, by the action of acids or alkalis, may be converted into the corresponding oxyacids, $C_nH_{2n}O_3$.

Ketones are not convertible by oxidation into acids containing the same number of carbon-atoms as themselves. When boiled with chromic acid mixture, they decompose in such a manner that the group CO separates in combination with the lower alcohol-radicle, and forms an acid; while, if the other radicle is a primary radicle it is likewise oxidised to an acid, normal or iso, according to the constitution of the radicle; thus:



$$\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3(CH_2)_3}\end{matrix}\right>\mathrm{CO} + \mathrm{O_3} = \mathrm{CH_3.CO.OH} + \mathrm{CH_3.(CH_2)_2.COOH}$$

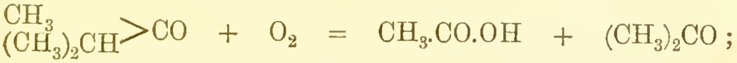
Methyl-butyl ketone. Acetic acid. Butyric acid



$$\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{(CH_3)_2CH.CH_2}\end{matrix}\right>\mathrm{CO} + \mathrm{O_3} = \mathrm{CH_3.CO.OH} + \mathrm{(CH_3)_2CH.COOH}$$

Methyl-isobutyl ketone. Acetic acid. Isobutyric acid.

If, on the other hand, the higher radicle is secondary, it will be oxidised to a ketone, which will be further split up by oxidation:



$$\left.\begin{matrix}\mathrm{CH_3}\\\mathrm{(CH_3)_2CH}\end{matrix}\right>\mathrm{CO} + \mathrm{O_2} = \mathrm{CH_3.CO.OH} + \mathrm{(CH_3)_2CO};$$

Methyl-isopropyl ketone. Acetic acid. Acetone.

and if the higher radicle is tertiary, such as $\mathrm{C(CH_3)_3}$, it will be immediately split up.*

Dimethyl Ketone.—Acetone, $\mathrm{CO(CH_3)_2}$.—This compound is formed:—1. By the dry distillation of acetates.—2. By oxidation of pseudopropyl alcohol.—3. By the action of water at 180°–200° on acetone chloride or bromide (p. 70):

$$\mathrm{CH_3.CCl_2.CH_3} + \mathrm{H_2O} = \mathrm{2HCl} + \mathrm{CH_3.CO.CH_3};$$

or on propene chloride (or bromide), $\mathrm{CH_3.CHCl.CH_2Cl}$ (in which case a molecular transposition of H and Cl must be supposed to take place in the first instance), or on monochloro- or monobromopropene:

$$\mathrm{CH_3{-}CCl{=}CH_2} + \mathrm{H_2O} = \mathrm{HCl} + \mathrm{CH_3.CO.CH_3}.$$

4. Together with other products, by passing the vapour of strong acetic acid through an iron tube heated to dull redness, and by the dry distillation of citric acid, tartaric acid, sugar, starch, gum, and wood: hence it occurs in crude wood-spirit.

Acetone is best prepared by the dry distillation of acetates, the calcium or the lead salt being the most convenient for the purpose. The crude distillate is saturated with potassium carbonate, and afterwards rectified in a water-bath from calcium chloride.

Pure acetone is a colourless limpid liquid, of peculiar odour: it has a density of 0·792, and boils at 55·5°: the density of its vapour (referred to air) is 2·022. Acetone is very inflammable, and burns with a bright flame: it is miscible in all proportions with water, alcohol, and ether.

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* See Watts's Dictionary of Chemistry, 2nd Supplement, 711.

Nascent hydrogen converts it into pseudopropyl alcohol (p. 143); but at the same time a portion of the acetone doubles its molecule, and likewise takes up hydrogen, being thereby converted into a crystalline substance, pinacone, $C_6H_{14}O_2 = 2C_3H_6O + H_2$.

By *oxidation* with chromic acid mixture, acetone is converted into acetic and formic acids, the latter being for the most part further oxidised to H_2O and CO_2.

$$\underset{\text{Acetone.}}{CH_3.CO.CH_3} + O_3 = \underset{\text{Acetic acid.}}{CH_3.CO.OH} + \underset{\text{Formic acid.}}{H.CO.OH}$$

Acetone treated with *hydrocyanic acid*, water, and hydrochloric acid is converted into oxyisobutyric (acetonic) acid:

$$(CH_3)_2CO + CHN + 2H_2O + HCl = NH_4Cl + (CH_3)_2COH.COOH,$$

By *phosphorus pentachloride*, acetone is converted into acetone chloride or methylchloracetol, $CH_3.CCl_2.CH_3$; similarly with PBr_5. With P_2S_5, it forms thioacetone, $CH_3.CS.CH_3$, a yellowish, offensive-smelling liquid, boiling at 183°–185°, insoluble in water.

Chlor- and *Brom-acetones.*—These compounds are formed by the direct action of chlorine and bromine on acetone, and in other ways.

Monochloracetone, $CH_3.CO.CH_2Cl$, is formed by passing chlorine into cold acetone, and by the action of hypochlorous acid on monochloro- or monobromopropene:

$$CH_3{-}CBr{=}CH_2 + ClOH = HBr + CH_3.CO.CH_2Cl.$$

It is a liquid, insoluble in water, boiling at 119°, and emitting vapours which excite a copious flow of tears.

Dichloracetones, $C_2H_4Cl_2O$.—Of these there are two, viz.:

$$\underset{\text{Unsymmetrical.}}{CH_3.CO.CHCl_2} \quad \text{and} \quad \underset{\text{Symmetrical.}}{CH_2Cl.CO.CH_2Cl}.$$

The former, produced by direct chlorination of acetone, is an oily liquid, having a density of 1·236 at 21°, and boiling at 120°.

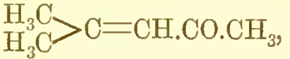
The symmetrical modification, obtained by oxidation of symmetrical dichlorhydrin, $CH_2Cl.CHOH.CH_2Cl$, crystallises in rhombic plates, melts at 43°, and boils at 172°–174°.

Condensation-products of Acetone.—When acetone is subjected to the action of dehydrating agents, such as sulphuric acid, quick-lime, zinc chloride, or hydrochloric acid, two or more molecules of it unite together, with separation of water, to form a condensation-product; thus:

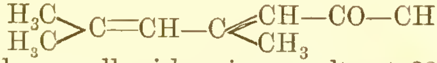
$$2C_3H_6O - H_2O = \underset{\text{Mesityl oxide.}}{C_6H_{10}O}$$

$$3C_3H_6O - 2H_2O = \underset{\text{Phorone.}}{C_9H_{14}O}$$

These bodies are best prepared by saturating acetone with gaseous hydrogen chloride, leaving the liquid to itself for some time, and treating the product with alcoholic potash. On dilution with water an oily liquid is obtained, consisting of mesityl oxide and phorone, which may be separated by fractional distillation.

Mesityl Oxide,  $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C{=}CH.CO.CH_3$, is a colourless oil, smelling like peppermint, and boiling at 130°. Treated with phosphorus pentachloride, it is converted into the chloride, $C_6H_{10}Cl_2$. By boiling with dilute sulphuric acid, it is resolved into two molecules of acetone.

An isomeric compound, called Metacetone, is formed by distilling sugar with lime; it is a liquid boiling at 84°.

Phorone, $C_9H_{14}O$, probably  $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C{=}CH{-}C\!\!<\!\!\begin{matrix}CH{-}CO{-}CH\\CH_3\end{matrix}$ —This body crystallises in large yellowish prisms, melts at 28°, boils at 196°, and when boiled with dilute sulphuric acid takes up water, and is resolved into 3 molecules of acetone:

$$C_9H_{14}O + 2H_2O = 3C_3H_6O.$$

Acetophorone, produced by heating acetone with quick lime, and camphophorone, obtained from camphoric acid, appear to be isomeric with the phorone obtained as above.

Acetone heated with strong *sulphuric acid* yields a distillate of mesitylene or trimethylbenzene, a body belonging to the aromatic group:

$$3C_3H_6O = 3H_2O + C_9H_{12}.$$

The same body is formed by the action of sulphuric acid on phorone. Other ketones heated with sulphuric acid likewise yield derivatives of benzene.

Acetonamines.*—Acetone, heated with ammonia, yields a mixture of three bases, the composition and mode of formation of which are indicated by the following formulæ:

Diacetonamine,	$C_6H_{13}NO = 2C_3H_6O + NH_3 - H_2O.$
Triacetonamine,	$C_9H_{17}NO = 3C_3H_6O + NH_3 - 2H_2O.$
Dehydrotriacetonamine,	$C_9H_{15}N = C_9H_{17}NO - H_2O.$

Diacetonamine is the chief product obtained at a moderate heat, and is best prepared by passing dry ammonia gas into a flask containing acetone in a state of gentle ebullition. It is a colourless liquid, having an ammoniacal odour and strong alkaline reaction; mixes in all proportions with water, alcohol, and ether, oxidises and turns brown on exposure to the air; forms crystalline salts with hydrochloric, sulphuric, and oxalic acids; the *platinochloride*, $2(C_6H_{13}NO.HCl).PtCl_4$, crystallises from water in orange-yellow monoclinic prisms containing 2 molecules H_2O.

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* Heintz, Liebig's Annalen, clxxiv. 133; clxxviii. 305, 326; clxxxiii. 276, 283. Sokoloff and Latschinoff.—*Deut. Chem.* Ges. Ber. vii. 1384.

Triacetonamine, $C_9H_{17}NO$, is the chief product obtained at higher temperatures, and is best prepared by boiling diacetonamine with acetone in a flask fitted with a reversed condenser. It crystallises in large colourless square tablets or long needles, having a faint ammoniacal and camphorous odour, and melting at 39·6°. It dissolves easily in water, alcohol, and ether; the aqueous solution has a strong alkaline reaction. It may be partly volatilised without decomposition at 100°, but decomposes at higher temperatures. The *hydrochloride*, $C_9H_{17}NO.HCl$, crystallises from alcohol in small needles. The *platinochloride*, $2(C_9H_{17}NO.HCl).PtCl_4 + 3H_2O$, forms tufts of long golden-yellow needles, easily soluble in water, sparingly in alcohol.

An uncrystallisable modification of triacetonamine, called isotriacetonamine, is contained in the mixture of bases formed by the action of ammonia on acetone. It forms a crystalline platinochloride containing $2H_2O$.

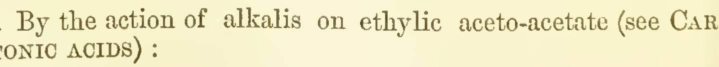
Dehydrotriacetonamine, $C_9H_{15}N$, is obtained by distilling the last mother-liquor of the same crude product with potash: it forms a platinum salt, $2(C_9H_{15}N.HCl).PtCl_4$, which crystallises in oblique rhombic prisms.

Dehydropentacetonamine, $C_{15}H_{23}N$, is obtained, amongst other products, by heating triacetonamine with hydrochloric acid:

$$5C_9H_{17}NO + 2HCl = 3C_{15}H_{23}N + 2NH_4Cl + 5H_2O.$$

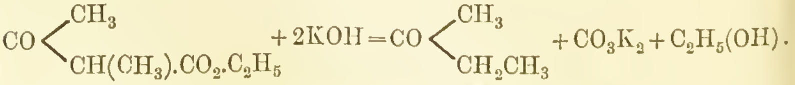
The hydrochloride forms small colourless crystals, slightly soluble in water. The free base separates as an oil on adding an alkali to the solution of the hydrochloride.

Methyl-ethyl Ketone, $C_4H_8O = CO{<}{\substack{CH_3 \\ C_2H_5}}$, is formed: 1. By oxidation of secondary butyl alcohol.—2. By the action of zinc-ethyl on acetyl chloride, or of zinc-methyl on propionyl chloride.—3. By distilling a mixture of propionate and acetate of calcium.—4. By oxidation of methyl-ethyl-oxalic acid (see Oxalic acid):



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}C{<}\begin{matrix}OH\\CO_2H\end{matrix} + O = CO_2 + H_2O + \begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CO.$$

4. By the action of alkalis on ethylic aceto-acetate (see Carboketonic acids):



$$CO{<}\begin{matrix}CH_3\\CH(CH_3).CO_2.C_2H_5\end{matrix} + 2KOH = CO{<}\begin{matrix}CH_3\\CH_2CH_3\end{matrix} + CO_3K_2 + C_2H_5(OH).$$

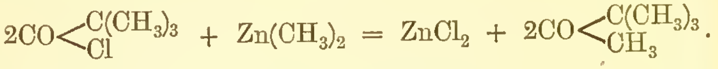
It is a fragrant liquid, of specific gravity 0·812 at 13°, boiling at 81°; unites with acid sulphites of alkali-metals; yields by oxidation two molecules of acetic acid.

The higher members of the series admit of isomeric modifications, the formula, $C_5H_{10}O$, including three, and $C_6H_{12}O$, six isomeric ketones.

The following table exhibits the specific gravities, boiling points, and products of oxidation of the best known ketones of the series:

KETONES.	Boiling Point.	Specific Gravity.	Products of Oxidation.
Dimethyl Ketone, $C_3H_6O=CO<\substack{CH_3\\CH_3}$	58°	0·814 at 6°	Formic and Acetic acids.
Methyl-ethyl Ketone, $C_4H_8O=CO<\substack{CH_3\\C_2H_5}$	81°	0·812 at 13°	Acetic acid (2 mol.)
Ketones, $C_5H_{10}O$:			
Methyl-propyl Ketone, $CO<\substack{CH_3\\(CH_2)(C_2H_5)}$	99–101°	0·807 at 18°	Acetic and Propionic acids.
Methyl-isopropyl Ketone, $CO<\substack{CH_3\\CH(CH_3)_2}$	93·5°	0·810 at 13°	
Diethyl Ketone or Propione, $CO<\substack{C_2H_5\\C_2H_5}$	101°	0·813 at 20°	Acetic and Propionic acids.
Ketones, $C_6H_{12}O$:			
Methyl-butyl Ketone, $CO<\substack{CH_3\\(CH_2)_3CH_3}$	127°	0·829 at 0°	Acetic and Butyric acids.
Methyl-isobutyl Ketone, $CO<\substack{CH_3\\CH_2.CH(CH_3)_2}$	114	0·819 at 0°	Acetic and Isobutyric acids.
Methyl-katabutyl Ketone, $CO<\substack{CH_3\\C(CH_3)_3}$	106°	0·823 at 0°	Acetic and Trimethylacetic acids.
Ethyl-propyl Ketone, $CO<\substack{C_2H_5\\(CH_2)_2(CH_3)}$	128°	0·833 at 0°	
Ketones, $C_7H_{14}O$:			
Dipropyl Ketone, $CO<\substack{C_3H_7\\C_3H_7}$	144°	0·82 at 20	Butyric and Propionic acids.
Di-Isopropyl Ketone, $CO<\substack{C_3H_7\\C_3H_7}$	123–124°	...	Isobutyric acid, Acetic acid, and CO_2.
Diethylacetone, $CO<\substack{CH_3\\CH(C_2H_5)_2}$	137–139°	0·817 at 22°	
Methyl-pentyl Ketone, $CO<\substack{CH_3\\C_5H_{11}}$	155–156°	0·813 at 20°	Acetic and normal Valeric acids.
Methyl-hexyl Ketone, $C_8H_{16}O = CO<\substack{CH_3\\C_6H_{13}}$	171°	0·818°	Acetic and Caproic acids.
Di-Isobutyl Ketone or Valerone, $C_9H_{18}O=CO(C_4H_9)_2$	182°	0·833 at 30°	
Ketones, $C_{11}H_{22}O$:			
Diamyl Ketone or Caprone, $CO(C_5H_{11})_2$	220°		
Methyl-nonyl Ketone, $CO<\substack{CH_3\\C_9H_{19}}$	225°	Melting pt. 15°	Acetic and Pelargonic acids.
Dihexyl Ketone or Œnanthone, $C_{12}H_{26}O = CO(C_6H_{13})_2$	255°	30°	
Diheptyl Ketone, $C_{15}H_{30}O = CO(C_7H_{15})_2$	280°	40°	
Dinonyl Ketone, $C_{19}H_{38}O = CO(C_9H_{19})_2$	350°	58°	

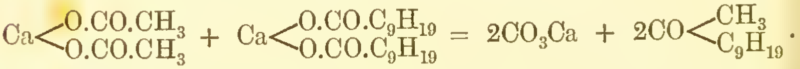
Methyl-katabutyl Ketone, $CH_3—CO—C(CH_3)_2$, is probably the compound called pinacolin, formed by heating pinacone, $C_6H_{14}O_2$ (p. 177), with hydrochloric or dilute sulphuric acid. It is likewise formed by the action of zinc-methyl on trimethacetyl chloride:



$$2CO\left<\begin{matrix}C(CH_3)_3\\Cl\end{matrix}\right. + Zn(CH_3)_2 = ZnCl_2 + 2CO\left<\begin{matrix}C(CH_3)_3\\CH_3\end{matrix}\right. .$$

Nascent hydrogen converts it into pinacolyl alcohol or methyl-katabutyl carbinol, $C(CH_3)_3—CHOH—CH_3$ (p. 155).

Methyl-nonyl Ketone, $CH_3—CO—C_9H_{19}$, is the chief constituent of oil of rue, and may be extracted therefrom by agitation with acid sodium sulphite. It is formed artificially by distilling a mixture of calcium acetate and rutate:



$$Ca\left<\begin{matrix}O.CO.CH_3\\O.CO.CH_3\end{matrix}\right. + Ca\left<\begin{matrix}O.CO.C_9H_{19}\\O.CO.C_9H_{19}\end{matrix}\right. = 2CO_3Ca + 2CO\left<\begin{matrix}CH_3\\C_9H_{19}\end{matrix}\right. .$$

It is an oily liquid, with a bluish fluorescence, solidifying at low temperatures to a laminar mass.

ORGANIC ACIDS.

Organic acids, or Carbon-acids, contain the univalent group, COOH or $O{=}\overset{|}{C}{-}OH$ (called carboxyl or oxatyl), linked by its free combining unit with a hydrocarbon residue, and they may be regarded as derived from hydrocarbons, saturated or unsaturated, by the substitution of one or more of these univalent groups for an equal number of hydrogen-atoms; thus:

from	CH_4	are derived	$CH_3—CO_2H$	and	$CH_2\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$
	Methane.		Acetic acid.		Malonic acid.
,,	C_2H_6	,,	$C_2H_5.CO_2H$	,,	$C_2H_4\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$
	Ethane		Propionic acid.		Succinic acid.
,,	C_3H_6	,,	$C_3H_5.CO_2H$	,,	$C_3H_4\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$
	Propene.		Crotonic acid.		Citraconic acid.

Many acids are formed by oxidation from primary alcohols, the H_2 of the groups CH_2OH in these alcohols being replaced by O; thus:

Alcohols.	*Acids.*	
CH_3 CH_2 CH_2OH Propyl alcohol.	CH_3 CH_2 $COOH$ Propionic acid.	
CH_2OH CH_2 CH_2OH β Propene glycol.	CH_2OH CH_2 $COOH$ β Lactic acid.	$COOH$ CH_2 $COOH$ Malonic acid.
CH_2OH $CHOH$ CH_2OH Glycerin.	CH_2OH $CHOH$ $COOH$ Glyceric acid.	$COOH$ $CHOH$ $COOH$ Oxymalonic acid.

An acid may, however, contain one or more hydroxyl groups not directly connected with the group CO, and the hydrogen in these groups, as well as in the group CO_2H, is replaceable by alcohol-radicles (also by alkali-metals) producing acid ethers, or alcoholic acids, *e.g.*, ethyl-lactic acid, $CH_2(OC_2H_5)—CH_2—CO.OH$.

The total number of hydroxyl groups in an organic acid is the same as that of the alcohol from which it is derived, and this determines the atomicity of the acid, and the number of ethers which it is capable of forming with any given alcohol-radicles; thus β-lactic acid, though it contains only one atom of basic hydrogen, and therefore forms only one class of metallic salts, represented by the formula $C_3H_5O_3M$, is diatomic, like propene-glycol, and can form two ethylic ethers, viz., ethyl-β-lactic acid and diethyl β-lactate or ethylic ethyl-lactate; thus:

CH_2OH CH_2 $COOH$ β-Lactic acid (monobasic).	$CH_2OC_2H_5$ CH_2 $COOH$ Ethyl-β-lactic acid (monobasic).	$CH_2OC_2H_5$ CH_2 $COOC_2H_5$ Diethylic β-lactate (neutral).

From these considerations it appears that monatomic acids must necessarily be monobasic; but diatomic acids may be either monobasic or bibasic; triatomic acids, either monobasic, bibasic, or tribasic; and so on.

Many of the most important acids are derived, in the manner above explained, from actually known alcohols; others, though they have no alcohols actually corresponding with them, are homologous with other acids derived from known alcohols; but there is also a considerable number of acids, especially those formed in the vegetable or animal organism, which cannot be regarded as derivatives of alcohols of any known series; but the number of these unclassified acids will doubtless diminish as their composition and reactions become more thoroughly known.

Acids may also be regarded as compounds of hydroxyl with oxygenated radicles (acid radicles) formed from the corresponding alcohol-radicles by substitution of O for H_2; *e.g.*,

$C_2H_5.OH$ Ethyl alcohol.	$C_2H_3O.OH$ Acetic acid.	
$C_3H_6(OH)_2$ Propene glycol.	$C_3H_4O(OH)_2$ Lactic acid.	$C_3H_2O_2(OH)_2$ Malonic acid.

The replacement of the hydroxyl in an acid by chlorine, bromine, or iodine, gives rise to acid chlorides, &c.; thus from acetic acid, $C_2H_3O(OH)$, is derived acetic chloride, C_2H_3OCl, &c. The replacement of the hydrogen within the radicle (radical hydrogen) by the same elements, or by the groups, CN, NO_2, NH_2, &c., gives rise to chlorinated, brominated, cyanated, nitrated, and amidated acids. Lastly, the replacement of the *extra-radical* or *typic* hydrogen by alcohol-radicles gives rise to ethereal salts of compound ethers; and its replacement by acid radicles yields acid oxides or anhydrides (p. 26). The derivatives of each acid will be described in connection with the acid itself.

Monatomic Acids.

These acids, being derived from monatomic alcohols by substitution of O for H_2, necessarily contain two atoms of oxygen. Each series of hydrocarbons yields a series of monatomic alcohols and a series of monatomic acids; thus:

Hydrocarbons.	Alcohols.	Acids.
C_nH_{2n+2}	$C_nH_{2n+2}O$	$C_nH_{2n}O_2$
C_nH_{2n}	$C_nH_{2n}O$	$C_nH_{2n-2}O_2$
C_nH_{2n-2}	$C_nH_{2n-2}O$	$C_nH_{2n-4}O_2$
C_nH_{2n-4}	$C_nH_{2n-4}O$	$C_nH_{2n-6}O_2$
&c.	&c.	&c.

The best known monatomic acids are those belonging to the series $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-8}O_2$, and $C_nH_{2n-10}O_2$. The last two belong to the aromatic group. Of the other series only a few terms have hitherto been obtained.

1. Acids of the Fatty Series,

$$C_nH_{2n}O_2 = C_{n-1}H_{2n-1}.CO_2H = C_nH_{2n-1}O.OH.$$

These acids are called Fatty or Adipic Acids, because most of them are of an oily consistence, and the higher members of the series are solid fats. The following is a list of the known members of the series:

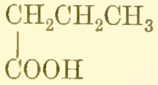
Formic acid, . . .	CH_2O_2	Lauric acid, ...	$C_{12}H_{24}O_2$
Acetic acid, ...	$C_2H_4O_2$	Myristic acid, . . .	$C_{14}H_{28}O_2$
Propionic acid, . .	$C_3H_6O_2$	Palmitic acid, . . .	$C_{16}H_{32}O_2$
Butyric acid (normal),	$C_4H_8O_2$	Margaric acid, . . .	$C_{17}H_{34}O_2$
Valeric acid „ .	$C_5H_{10}O_2$	Stearic acid,. . . .	$C_{18}H_{36}O_2$
Caproic acid „ .	$C_6H_{12}O_2$	Arachidic acid, . . .	$C_{20}H_{40}O_2$
Œnanthylic acid, . .	$C_7H_{14}O_2$	Behenic acid, . . .	$C_{22}H_{44}O_2$
Caprylic acid, . . .	$C_8H_{16}O_2$	Cerotic acid, . . .	$C_{27}H_{54}O_2$
Pelargonic acid, . .	$C_9H_{18}O_2$	Melissic acid, . . .	$C_{30}H_{60}O_2$
Rutic or Capric acid, .	$C_{10}H_{20}O_2$		

The higher members, from valeric acid upwards, are sometimes denoted by names indicating their number of carbon-atoms, and the alcohols from which they are derived, *e.g., pentoic, hexoic, heptoic,* &c.

The acid radicles in the formula, $C_nH_{2n-1}(OH)$ may be regarded as compounds of carbonyl CO, with alcohol-radicles: $C_nH_{2n-1}O = CO(C_{n-1}H_{2n-1})$, and accordingly the several acids may be formulated as follows :

$COH.OH$	$CO(CH_3).OH$	$CO(C_2H_5)OH$
Formic.	Acetic.	Propionic.

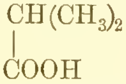
All the acids of the series containing more than three carbon-atoms admit of isomeric modifications, according to the constitution of the alcohol-radicles which they contain: butyric acid, $C_5H_8O_2$, for example may exhibit the following modifications:



$$\begin{matrix} CH_2CH_2CH_3 \\ | \\ COOH \end{matrix}$$

Normal butyric acid.

or



$$\begin{matrix} CH(CH_3)_2 \\ | \\ COOH \end{matrix}$$

Isobutyric acid.

But none of these acids can exhibit modifications analogous to the secondary and tertiary alcohols: because in them the carbon-atom which is associated with hydroxyl has two of its other units of equivalence satisfied by an atom of bivalent oxygen, and therefore cannot unite directly with more than one other atom of carbon. Accordingly, it is found that the secondary and tertiary alcohols are not converted by oxidation into acids containing the same number of carbon-atoms as themselves.

Occurrence.—Most of the fatty acids are found in the bodies of plants or animals, some in the free state ; formic acid in ants and nettles ; valeric acid in valerian root ; pelargonic acid in the essential oil of *Pelargonium roseum ;* and cerotic acid in bees'-wax. Others occur as ethereal salts of monatomic or polyatomic alcohols : as cetyl palmitate in spermaceti ; ceryl cerotate in Chinese wax ; glyceric butyrate, palmitate, stearate, &c., in natural fats.

Formation.—1. By oxidation of the primary alcohols of the methyl series, as by exposure to the air in contact with platinum black, or by heating with aqueous chromic acid.—2. By the oxidation of aldehydes. In this case an atom of oxygen is simply added ; *e.g.,* C_2H_4O (aldehyde) $+ O = C_2H_4O_2$ (acetic acid).

3. By the action of carbon dioxide on the potassium or sodium compound of an alcohol-radicle of the methyl series; thus:

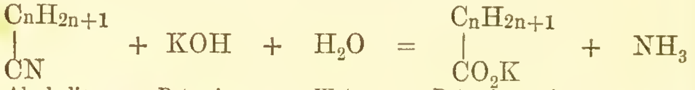
$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Sodium methide.}}{CH_3Na} = \underset{\text{Sodium acetate.}}{CH_3.CO_2Na}$$

4. By heating the ethylate of an alkali-metal in alcoholic solution with carbon monoxide under pressure: *e.g.*,

$$\underset{\text{Potassium ethylate.}}{C_2H_5OK} + CO = \underset{\text{Potassium acetate.}}{C_2H_5.CO.OK.}$$

This reaction, however, is slow, and yields but a small product.

5. By the action of alkalis or acids on the cyanides of the alcohol-radicles, C_nH_{2n+1}; thus:



$$\underset{\text{Alcoholic cyanide.}}{\begin{matrix}C_nH_{2n+1}\\ |\\ CN\end{matrix}} + \underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium-salt of fatty acid.}}{\begin{matrix}C_nH_{2n+1}\\ |\\ CO_2K\end{matrix}} + \underset{\text{Ammonia.}}{NH_3}$$

and:

$$\underset{\text{Alcoholic cyanide.}}{C_nH_{2n+1}.CN} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium salt.}}{C_nH_{2n+1}.CO_2H} + \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

In this manner the cyanide of each alcohol-radicle yields the potassium salt of the acid next higher in the series, that is, containing one atom of carbon more; methyl cyanide, for example, yielding acetic acid, ethyl cyanide yielding propionic acid, &c.: thus:

$$\underset{\text{Methyl cyanide.}}{CH_3.CN} + KOH + H_2O = \underset{\text{Potassium acetate.}}{CH_3.CO_2K} + NH_3$$

6. By the action of water on the corresponding acid chlorides: *e.g.*,

$$\underset{\text{Acetyl chloride.}}{C_2H_3OCl} + HOH = HCl + \underset{\text{Acetic acid.}}{C_2H_3O(OH)}$$

Now, these acid chlorides can be produced, in some instances at least, by the action of carbonyl chloride (phosgene gas) on the corresponding paraffins; thus:

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Carbonyl chloride.}}{COCl_2} = HCl + \underset{\text{Acetyl chloride.}}{C_2H_3OCl};$$

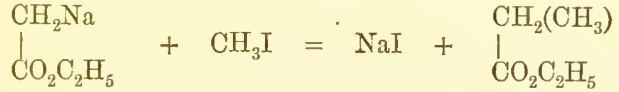
$$\underset{\text{Butane.}}{C_4H_{10}} + \underset{\text{Carbonyl chloride.}}{COCl_2} = HCl + \underset{\text{Valeryl chloride.}}{C_5H_9OCl}$$

By these combined reactions, therefore, the paraffins may be converted into the corresponding fatty acids.

7. By the action of phosgene on the zinc-compounds of the alcohol-radicles, whereby acid chlorides are formed, to be subsequently decomposed by water:

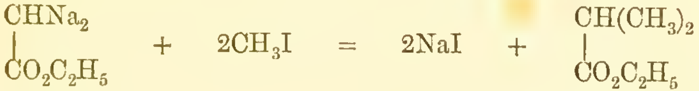
$$\underset{\text{Zinc-methyl.}}{Zn(CH_3)_2} + 2COCl_2 = ZnCl_2 + \underset{\text{Acetyl chloride.}}{2(CH_3.COCl)}$$

8. By dissolving sodium in methylic or ethylic acetate, adding the iodide of an alcohol radicle, heating the mixture to 100° and distilling. The reaction, which is complex, and will be more fully explained hereafter (see CARBO-KETONIC ACIDS), may be viewed—so far as our present purpose is concerned—as consisting in the substitution of 1 or 2 atoms of sodium for hydrogen in the methyl-group of acetic acid, and the decomposition of the resulting compound by the alcoholic iodide: *e.g.*,



$$\begin{array}{l}CH_2Na\\ |\\ CO_2C_2H_5\end{array} + CH_3I = NaI + \begin{array}{l}CH_2(CH_3)\\ |\\ CO_2C_2H_5\end{array}$$

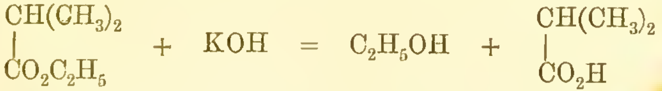
Ethylic sodacetate. Ethylic methyl acetate.



$$\begin{array}{l}CHNa_2\\ |\\ CO_2C_2H_5\end{array} + 2CH_3I = 2NaI + \begin{array}{l}CH(CH_3)_2\\ |\\ CO_2C_2H_5\end{array}$$

Ethylic disodacetate. Ethylic dimethyl acetate.

The resulting ethers saponified with caustic potash yield the free acids; thus:



$$\begin{array}{l}CH(CH_3)_2\\ |\\ CO_2C_2H_5\end{array} + KOH = C_2H_5OH + \begin{array}{l}CH(CH_3)_2\\ |\\ CO_2H\end{array}$$

Ethylic dimethyl-acetate. Alcohol. Dimethylacetic or Isobutyric acid.

Ethyl-acetic or normal butyric acid, $CH_2(C_2H_5)—CO_2H$, and other members of the series, may be obtained in a similar manner.

The eight modes of formation above given are general, or capable of being made so. There are also special methods of producing particular acids of the series, but in most of these cases the reactions cannot be distinctly traced; thus formic, acetic, propionic, butyric, and valeric acids are produced by the oxidation of albumin, fibrin, casein, gelatin, and other similar substances; propionic and butyric acids, in certain kinds of fermentation; acetic acid by the destructive distillation of wood and other vegetable substances.

Properties.—Most of the fatty acids are, at ordinary temperatures, transparent and colourless liquids; formic and acetic acids are watery; propionic acid and the higher acids, up to pelargonic acid, are oily; rutic acid and those above it are solid at ordinary temperatures, most of them being crystalline fats; cerotic and melissic acids are of waxy consistence.

Reactions.—1. When the fatty acids are submitted to the action of *nascent oxygen* evolved by electrolysis, the carboxyl (COOH) contained in them is resolved into water and carbon dioxide, and the alcohol-radicle is set free (p. 40); thus:

$$\underset{\text{Valeric acid.}}{2(C_4H_9.CO_2H)} + O = H_2O + 2CO_2 + \underset{\text{Dibutyl.}}{C_4H_9.C_4H_9}$$

2. When the ammonium salt of either of these acids is heated with *phosphoric oxide*, it gives up water, and is converted into the cyanide of the alcohol-radicle next below it; *e.g.*, ammonium acetate into methyl cyanide:

$$CH_3—COONH_4 - 2H_2O = CH_3—CN.$$

This reaction is the converse of the fifth mode of formation above given.

3. By distilling the potassium salt of a fatty acid with an equivalent quantity of *potassium formate*, the corresponding aldehyde is obtained:

$$\underset{\text{Acetate.}}{CH_3.CO.OK} + \underset{\text{Formate.}}{H.CO.OK} = \underset{\text{Aldehyde.}}{CH_3.COH} + \underset{\text{Carbonate.}}{K_2CO_3};$$

and the aldehyde, treated with nascent hydrogen, is converted into a primary alcohol (pp. 117, 245).

4. By subjecting the barium or calcium salt of a fatty acid to dry distillation, a similar decomposition takes place, resulting in the formation of a ketone; and the ketone, treated with nascent hydrogen, yields a secondary alcohol (pp. 117, 259).

By these reactions, the fatty acids may be converted into alcohols.

5. The fatty acids, heated with *alcohols* in sealed tubes, yield compound ethers, or ethereal salts, water being eliminated:

$$\underset{\substack{\text{Butyric}\\\text{acid.}}}{C_4H_7O(OH)} + \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{HOC_2H_5} = H_2O + \underset{\substack{\text{Ethyl}\\\text{butyrate.}}}{C_4H_7O(OC_2H_5)}$$

The conversion, however, is never complete, a portion, both of the acid and of the alcohol, remaining unaltered, in whatever proportion they may be mixed (p. 112).

The ethereal salts of the fatty acids are, for the most part, more easily obtained by acting upon the alcohol with an acid chloride, or by passing hydrochloric acid gas into a solution of the fatty acid in the alcohol; thus butyric chloride and ethyl alcohol yield ethyl-butyrate:

$$C_4H_7OCl + HOC_2H_5 = HCl + C_4H_7O(OC_2H_5).$$

Another method very commonly adopted, is to distil a potassium salt of the fatty acid with a mixture of the alcohol and strong sulphuric acid. In this case an acid sulphuric ether is first formed (as ethyl-sulphuric acid from ethyl alcohol, p. 136), and this acts upon the salt of the fatty acid in the manner illustrated by the equation:

$$SO_2(HO)OC_2H_5 + C_4H_7O(OK) = C_4H_7O(OC_2H_5) + SO_2(OH)(OK)$$

Ethyl-sulphuric acid. Potassium butyrate. Ethyl butyrate. Acid potassium sulphate.

The ethereal salts of the fatty acids are either volatile, oily or syrupy liquids, or crystalline solids, for the most part insoluble in water, but soluble in alcohol and in ether. When distilled with potash or soda, they take up water and are saponified, that is to say, resolved into the alcohol and acid; *e.g.*, ethyl butyrate into butyric acid and ethyl alcohol:

$$C_4H_7O(OC_2H_5) + HOH = C_4H_7O(OH) + C_2H_5(OH).$$

6. The fatty acids are strongly acted upon by the *chlorides, bromides, oxychlorides,* and *oxybromides of phosphorus,* yielding acid chlorides and bromides, the phosphorus being at the same time converted into phosphorous or phosphoric acid; thus:

$$3C_2H_3O(OH) + PCl_3 = PO_3H_3 + 3C_2H_3OCl.$$
$$3C_2H_3O(OH) + PCl_3O = PO_4H_3 + 3C_2H_3OCl.$$
$$C_2H_3O(OH) + PCl_5 = PCl_3O + HCl + C_2H_3OCl.$$

These acid chlorides are, for the most part, oily liquids, having a pungent acid odour; they are easily decomposed by water, yielding the fatty acid and hydrochloric acid. This decomposition takes place also when they are exposed to the air: hence they emit dense acid fumes. They react in an exactly similar manner with alcohols, as above-mentioned, yielding hydrochloric acid and a compound ether.

7. The chlorides of the acid radicles, $C_nH_{2n+1}O$, act violently on ammonia, forming ammonium chloride and the corresponding amides, acetic chloride, for example, yielding acetamide:

$$C_2H_3OCl + 2NH_3 = NH_4Cl + NH_2(C_2H_3O).$$

8. The acid chlorides, distilled with a metallic salt of the corresponding acid, yield a metallic chloride and the oxide or anhyride corresponding with the acid; thus:

$$C_2H_3OCl + C_2H_3O(OK) = KCl + (C_2H_3O)_2O.$$

In like manner, when distilled with the potassium salt of another onatomic acid, they yield oxides or anhydrides containing two onatomic acid radicles: *e.g.*,

$$C_2H_3OCl + C_7H_5O(OK) = KCl + \left.\begin{matrix} C_2H_3O \\ C_7H_5O \end{matrix}\right\} O$$

Acetic chloride. Potassium benzoate. Aceto-benzoic oxide.

The oxides of the fatty acid radicles may also be prepared by heating a dry lead-salt of the acid, in a sealed tube with carbon bisulphide; *e.g.*,

$$\underset{\text{Lead acetate.}}{2Pb\left\{\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix}\right.} + CS_2 = 2PbS + CO_2 + \underset{\text{Acetic oxide.}}{2(C_2H_3O)_2O}$$

The oxides of the fatty acid radicles are gradually decomposed by water, quickly when heated, yielding two molecules of the corresponding acid:

$$(C_2H_3O)_2O + H_2O = 2C_2H_3O(OH).$$

Those containing two acid radicles yield one molecule of each of the corresponding acids.

In contact with *alcoholic oxides* (*oxygen-ethers*), the acid oxides are converted into ethereal salts:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl oxide.}}{(C_2H_5)_2O} = \underset{\text{Ethyl acetate.}}{2C_2H_3O(OC_2H_5)}$$

With *alcohols*, in like manner, they yield a mixture of a compound ether with the acid:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)} = \underset{\text{Ethyl acetate.}}{C_2H_3O(OC_2H_5)} + \underset{\text{Acetic acid.}}{C_2H_3O(OH)}$$

The acid oxides are decomposed by *ammonia gas*, yielding a mixture of an ammonium-salt with an amide; *e.g.*,

$$(C_2H_3O)_2O + 2NH_3 = C_2H_3O(ONH_4) + NH_2C_2H_3O.$$

9. The fatty acids, subjected to the action of *chlorine* or *bromine*, give off hydrochloric or hydrobromic acid, and are converted into substitution-compounds containing one or more atoms of chlorine or bromine in place of hydrogen; but it is only the hydrogen within the radicle that can be thus exchanged, not that belonging to the hydroxyl group (the so-called *typic* hydrogen), so that the number of chlorine or bromine-atoms introduced in place of hydrogen is always less by at least one than the number of hydrogen-atoms in the acid:

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + Cl_2 = HCl + \underset{\text{Chloracetic acid.}}{C_2H_2ClO(OH)}$$

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + 3Cl_2 = 3HCl + \underset{\text{Trichloracetic acid.}}{C_2Cl_3O(OH)}$$

The iodated acids of the same series (or rather their ethereal salts) are obtained by heating the corresponding bromine-compounds with potassium iodide:

$$\underset{\text{Ethyl-brom-acetate.}}{C_2H_2BrO(OC_2H_5)} + KI = KBr + \underset{\text{Ethyl-iodacetate.}}{C_2H_2IO(OC_2H_5)};$$

and the ethers treated with potash yield potassium salts of the iodated acids, from which the acids may be obtained by decomposition with sulphuric acid.

10. The chlorinated and brominated fatty acids, boiled with *water* and *silver oxide*, exchange the whole of their chlorine or bromine for an equivalent quantity of hydroxyl, producing new acids, which differ from the primitive acids by a number of atoms of oxygen equal to the number of atoms of chlorine or bromine present; *e.g.*,

$$\underset{\text{Bromacetic acid.}}{2C_2H_3BrO_2} + Ag_2O + H_2O = 2AgBr + \underset{\text{Glycollic acid.}}{2C_2H_4O_3}$$

$$\underset{\text{Dibromobutyric acid.}}{C_4H_6Br_2O_2} + Ag_2O + H_2O = 2AgBr + \underset{\text{Dioxybutyric acid}}{C_4H_8O_4},$$

Dichloracetic and trichloracetic acid are not sufficiently stable to exhibit this transformation, their molecules splitting up altogether when boiled with silver oxide.

11. The monochlorinated and monobrominated acids, subjected to the action of an alcoholic solution of *ammonia gas*, yield ammonium chloride and a new acid, in which the chlorine or bromine is replaced by amidogen. Thus monochloracetic acid yields amidacetic acid, or glycocine:

$$C_2H_3ClO_2 + 2NH_3 = NH_4Cl + C_2H_3(NH_2)O_2 .$$

There is another way of viewing these amidated acids, which will be considered hereafter.

Formic acid, $CH_2O_2 = CHO(OH) = H.CO.OH$.—This acid occurs in the concentrated state in the bodies of ants, in the hairs and other parts of certain caterpillars, and in stinging nettles. It may be produced by the first, second, and fourth of the above-mentioned general methods of forming the fatty acids—viz., by the slow oxidation of methyl alcohol, or of formic aldehyde, in contact with platinum black, and as a potassium salt by heating hydrocyanic acid (hydrogen cyanide) with an alcoholic solution of potash:

$$HCN + KOH + H_2O = NH_3 + CHO(OK) .$$

It is also produced by certain special reactions—viz., 1. By passing carbon monoxide over moist potassium hydroxide, the gas being thereby absorbed, and producing potassium formate:

$$CO + HOK = COH(OK) .$$

The absorption of the gas is accelerated by the presence of a considerable quantity of water, and still more by alcohol or ether.

2. By passing carbon dioxide and water-vapour over potassium

at a moderate heat, acid potassium carbonate, $KHCO_3$, being formed at the same time :

$$K_2 + 2CO_2 + H_2O = KHCO_3 + KCHO_2.$$

3. By the action of sodium-amalgam on a strong solution of ammonium carbonate, and by boiling zinc-dust (a mixture of metallic zinc, oxide, and hydrate), or zinc carbonate with potash solution. In both these cases the production of formic acid is due to the nascent hydrogen, which, in presence of the alkali, unites with the CO_2 of the carbonate :

$$CO_2 + KOH + H_2 = HCO_2K + H_2O.$$

4. By distilling dry oxalic acid either alone or mixed with sand or pumice-stone, or better, with glycerin :

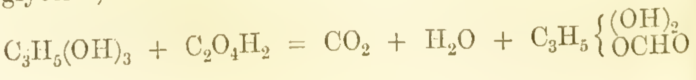
$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

5. By boiling chloroform with alcoholic solution of potash :

$$HCCl_3 + 4KOH = 3KCl + 2H_2O + H.CO.OK.$$

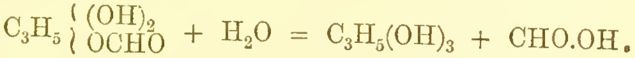
6. By the oxidation of sugar, starch, gum, and organic substances in general. This reaction affords a convenient method of preparing the acid :—1 part of sugar, 3 parts of manganese dioxide, and 2 parts of water, are mixed in a very capacious retort, or large metal still; 3 parts of oil of vitriol, diluted with an equal weight of water, are then added, and when the first violent effervescence from the disengagement of carbon dioxide has subsided, heat is cautiously applied, and a considerable quantity of liquid distilled over. This is very impure : it contains a volatile oily matter, and some substance which communicates a pungency not proper to formic acid in that dilute state. The acid liquid is neutralised with sodium carbonate, and the resulting formate purified by crystallisation, and, if needful, by animal charcoal. From this, or any other of its salts, solution of formic acid may be readily obtained by distillation with sulphuric acid.

The best mode of preparation, however, consists in heating oxalic acid in contact with glycerin. Very concentrated glycerin is added to crystallised oxalic acid, $C_2H_2O_4 + 2H_2O$, and the mixture is heated to 100°-110°, whereupon carbon dioxide escapes, and dilute formic acid distils over. As soon as the evolution of gas ceases, more oxalic acid is added, and the heating continued, whereupon a stronger formic acid distils over, and on further addition of oxalic acid, and heating, an acid of constant strength (56 per cent.) passes over. The course of the reaction is as follows : The crystallised oxalic acid, when heated, gives up its water, and the remainder forms with the glycerin, the monoformic ether of glycerin, or monoformin :



$$C_3H_5(OH)_3 + C_2O_4H_2 = CO_2 + H_2O + C_3H_5\left\{\begin{matrix}(OH)_2\\ OCHO\end{matrix}\right. ;$$

and the oxalic acid afterwards added is likewise resolved into anhydrous acid and water, which decomposes the formin into glycerin and formic acid :



$$C_3H_5\left\{\begin{matrix}(OH)_2\\ OCHO\end{matrix}\right. + H_2O = C_3H_5(OH)_3 + CHO.OH.$$

The regenerated glycerin reacts with the anhydrous oxalic acid, reproducing monoformin.

To obtain the acid in its most concentrated state, the dilute acid is saturated with lead oxide, the liquid is evaporated to complete dryness, and the dried lead formate, reduced to fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry sulphuretted hydrogen gas is passed.

Pure anhydrous formic acid is a clear, colourless liquid, which fumes slightly in the air, has an exceedingly penetrating odour, boils at about 100°,* and crystallises in large brilliant plates when cooled below 0°. The specific gravity of the acid is 1·233. Its vapour is inflammable, and burns with a blue flame. Concentrated formic acid is extremely corrosive, attacking the skin, and forming a blister or an ulcer, painful and difficult to heal.

Formic acid mixes in all proportions with water, alcohol, and ether. The aqueous acid has an odour and taste much resembling those of acetic acid : it reddens litmus strongly, and decomposes alkaline carbonates with effervescence.

Formic acid also unites with water in definite proportion, forming a hydrate, $CH_2O_2+H_2O$, which remains liquid at low temperatures, and distils at 106°. This hydrate may be regarded as a triatomic acid, viz., orthoformic acid, $HC(OH)_3$.

Formic acid is a powerful reducing agent. It may be readily distinguished from acetic acid by heating it with solution of *silver nitrate;* the metal is thus reduced, sometimes in the pulverulent state, sometimes as a specular coating on the glass tube, and carbon dioxide is evolved. Mercuric chloride is reduced by formic acid to calomel.

Formic acid heated with *oil of vitriol* splits up into water and carbon monoxide, $CH_2O_2=H_2O+CO$.

Chlorine converts it into hydrochloric acid and carbon dioxide :

$$CH_2O_2 + Cl_2 = 2HCl + CO_2.$$

Formic acid heated with strong *bases* is converted into oxalic acid, with disengagement of hydrogen; *e.g.*,

$$2CH_2O_2 + BaO = C_2BaO_4 + H_2 + H_2O.$$

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* At 98·5° (Liebig); 100° (Person); 101·1° (Roscoe); 105·5° (Kopp).

Formates.—The composition of these salts is expressed by the ormulæ, $MCHO_2$, $M''(CHO_2)_2$, $M'''(CHO_2)_3$, &c., according to the equivalent value of the metal or other positive radicle contained in them. They are all soluble in water; their solutions form dark-red mixtures with ferric salts. When distilled with strong sulphuric acid, they give off carbon monoxide and leave a residue of sulphate. The formates of the alkali-metals heated with the corresponding salts of other fatty acids, yield a carbonate and an aldehyde (p. 245).

Sodium formate crystallises in rhombic prisms containing $CHO_2Na.aq$. It reduces many metallic oxides when fused with them. *Potassium formate*, CHO_2K, is difficult to crystallise, on account of its great solubility. *Ammonium formate* crystallises in square prisms: it is very soluble, and is decomposed at high temperatures into hydrocyanic acid and water, the elements of which it contains: $CHO_2NH_4 = 2H_2O + CNH$. The formates of *barium*, *strontium*, *calcium*, and *magnesium* form small, prismatic, easily soluble crystals. *Lead formate* crystallises in small, diverging, colourless needles, which require for solution 40 parts of cold water. The *manganous, ferrous, zinc, nickel*, and *cobalt formates* are also crystallisable. *Cupric formate* is very beautiful, crystallising in bright blue rhombic prisms of considerable size. *Silver formate* is white, but slightly soluble, and decomposed by the least elevation of temperature.

Methyl formate, $CHO_2.CH_3$, metameric with acetic acid, is prepared by heating in a retort equal weights of neutral methyl sulphate and sodium formate. It is a very volatile liquid, lighter than water, boiling between 36° and 38°.

Ethyl formate, $CHO_2.C_2H_5$, metameric with methyl acetate and propionic acid (p. 30), is prepared by distilling a mixture of 7 parts of dry sodium formate, 10 of oil of vitriol, and 6 of strong alcohol. The formic ether, separated by the addition of water to the distilled product, is agitated with a little magnesia, and left for several days in contact with calcium chloride. Ethyl formate is colourless, has an aromatic odour, a density of 0·915, and boils at 56°. Water dissolves it to a small extent.

Ethyl Orthoformate, $HC(OC_2H_5)_3$, is produced by heating chloroform with sodium ethylate in alcoholic solution:

$$HCCl_3 + 3C_2H_5ONa = 3NaCl + HC(OC_2H_5)_3.$$

It is a liquid having an aromatic odour, boiling at 146°, insoluble in water. When heated with glacial acetic acid it is resolved into formate and acetate of ethyl.

Acetic Acid, $C_2H_4O_2 = C_2H_3O(OH) = CH_3(COOH)$.—This acid is found in small quantities in the juices of plants and in animal fluids. It may be produced by either of the first seven general methods of formation given on pages 269–271, and in particular by the slow oxidation of alcohol. When spirit of wine is dropped upon platinum black, the oxygen condensed in the pores of the latter reacts so powerfully upon the alcohol as to cause its instant inflammation. When the spirit is mixed with a little water, and slowly dropped upon the finely divided metal, oxidation still takes place, but with less energy, and vapour of acetic acid is abundantly evolved. In all these modes of formation, the acetic acid is ultimately producible from inorganic materials. It is also formed by the action of nascent hydrogen on trichloracetic acid, which may itself be produced from inorganic materials. Lastly, acetic acid is obtained, together with many other products, in the destructive distillation of wood and other vegetable substances.

Preparation.—1. Dilute alcohol, mixed with a little yeast, or almost any azotised organic matter susceptible of putrefaction, and exposed to the air, speedily becomes oxidised to acetic acid. Acetic acid is thus manufactured in Germany, by suffering such a mixture to flow over wood shavings steeped in a little vinegar, contained in a large cylindrical vessel through which a current of air is made to pass. The greatly extended surface of the liquid expedites the change, which is completed in a few hours. No carbonic acid is produced in this reaction.

The best vinegar is made from wine by spontaneous acidification in a partially filled cask to which the air has access. Vinegar is first introduced into the empty vessel, and a quantity of wine added; after some days, a second portion of wine is poured in, and after similar intervals, a third and a fourth. When the whole has become vinegar, a quantity is drawn off equal to that of the wine employed, and the process is recommenced. The temperature of the building is kept up to 30°. Such is the plan adopted at Orleans. In England vinegar is prepared from a kind of beer made for the purpose. The liquor is exposed to the air in half-empty casks, loosely stopped, until acidification is complete. Frequently a little sulphuric acid is afterwards added, with the view of checking further decomposition, or *mothering*, by which the product would be spoiled.

When dry, hard wood, as oak and beech, is subjected to destructive distillation at a red heat, acetic acid is found among the liquid condensable products of the operation. The distillation is conducted in a large iron cylinder to which a worm or condenser is attached; a sour, watery liquid, a quantity of tar, and much inflammable gas pass over, while charcoal of excellent quality remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the preparation of wood-spirit. The remainder is saturated with lime, concentrated by evaporation, and mixed with the solution of sodium sulphate; calcium sulphate is thereby precipitated, while the acetic acid is transferred to the soda. The filtered solution is evaporated to its crystallising point; and the crystals are drained as much as possible from the dark, tarry mother-liquor, and deprived by heat of their combined water. The dry salt is then cautiously fused, by which the last portions of tar are decomposed or expelled: it is then re-dissolved in water, and recrystallised. Pure sodium acetate, thus obtained, readily yields acetic acid by distillation with sulphuric acid.

The strongest acetic acid is prepared by distilling finely powdered anhydrous sodium acetate with three times its weight of strong sulphuric acid. The liquid is purified by rectification to free it from sodium sulphate accidently thrown up, and exposed to a low temperature. Crystals of pure acetic acid, $C_2H_4O_2$, then form in large quantity: they may be drained from the weaker fluid portion, and suffered to melt. Below 15·5° this substance, often called *glacial acetic acid*, forms large, colourless, transparent crystals, which above that temperature fuse to a thin, colourless liquid, of exceedingly pungent and well-known odour; it raises blisters on the skin. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. When diluted it has a pleasant acid taste. Glacial acetic acid in the liquid state has a density of 1·063, and boils at 120°. Its vapour is inflammable, and exhibits the variations of density already noticed (i. 253). At 300°, or above, it is 2·08 compared with air, or 30° compared with hydrogen, agreeing exactly with the theoretical density, which is half the molecular weight; but at temperatures near the boiling point it is considerably greater, being 2·90 at 140°, and 3·20 at 125° (referred to air).

Dilute acetic acid, or distilled vinegar, used in pharmacy, should always be carefully examined for copper and lead; these impurities are contracted from the metallic vessel or condenser sometimes employed in the process. The strength of any sample of acetic acid cannot be safely inferred from its density, but it is easily determined by observing the quantity of dry sodium carbonate necessary to saturate a known weight of the liquid. Common vinegar contains from 5 to 15 per cent. of the pure acid.

Acetic acid exhibits all the reactions of the fatty acids in general (pp. 272–275). The acid itself does not readily conduct the electric current, but a solution of potassium acetate is decomposed by electrolysis, with formation of dimethyl, or ethane, and potassium carbonate:

$$2(CH_3.CO.OK) + H_2O = C_2H_6 + H_2 + CO_2 + CO(OK)_2.$$

Acetic acid is not attacked by nitric acid, but *periodic acid* converts it by oxidation into formic acid and carbon dioxide, being itself reduced to iodic acid or even to free iodine:

$$C_2H_4O_2 + O_3 = CH_2O_2 + CO_2 + H_2O.$$

Potassium acetate distilled with *arsenious oxide* gives off a highly inflammable and characteristically fetid oil, consisting chiefly of arsendimethyl or cacodyl, $As_2(CH_3)_4$.

Acetates.—Acetic acid forms a large number of highly important salts, represented by the formulæ, $MC_2H_3O_2$, $M''(C_2H_3O_2)_2$, or $M'''(C_2H_3O_2)_3$, according to the equivalent value of the metal contained in them. Being a monobasic acid, it cannot form any acid salts properly so called, that is, by replacement of a *part* of its typic hydrogen (p. 268); but the normal acetates of the alkali-metals can take up a molecule of acetic acid, just as they take up water of crystallisation, forming salts called acid acetates or diacetates, $MC_2H_3O_2.C_2H_4O_2$. There are also basic acetates, formed by the union of a molecule of a normal acetate with a molecule of metallic oxide or hydrate.

POTASSIUM ACETATES.—The *normal salt*, $KC_2H_3O_2$, crystallises with great difficulty: it is generally met with as a foliated, white, crystalline mass, obtained by neutralising potassium carbonate with acetic acid, evaporating to dryness, and heating the salt to fusion. It is extremely deliquescent, and soluble in water and alcohol: the solution is usually alkaline, from a little loss of acid by the heat to which it has been subjected. From the alcoholic solution, potassium carbonate is thrown down by a stream of carbon dioxide.

The *acid salt*, $KC_2H_3O_2.C_2H_4O_2$, is formed by evaporating a solution of the neutral salt in excess of acetic acid, and crystallises by slow evaporation in long flattened prisms. It is very deliquescent, and decomposes at 200°, giving off crystallisable acetic acid.

SODIUM ACETATE, $NaC_2H_3O_2+3$ aq.—The mode of preparation of this salt on the large scale has been already described: it forms large, transparent, colourless crystals, derived from a rhombic prism, which are easily rendered anhydrous by heat, effloresce in dry air, and dissolve in 3 parts of cold, and in an equal weight of hot water; it is also soluble in alcohol. The taste of this salt is cooling and saline. The dry salt melts at 288°, and begins to decompose at 315°.

AMMONIUM ACETATES.—The *neutral acetate*, $NH_4C_2H_3O_2$, is a white odourless salt, obtained by saturating glacial acetic acid with dry ammonia gas. It is very difficult to obtain in the crystalline form, for its aqueous solution, when evaporated, gives off ammonia, and leaves the acid salt. When distilled with phosphoric oxide, it loses 2 molecules of water, and gives off ethenyl nitrile or acetonitrile, $(C_2H_3)N = NH_4C_2H_3O_2 - 2H_2O$. The aqueous solution, known in the Pharmacopœia as *Spiritus Mindereri*, is prepared by saturating aqueous acetic acid with ammonia or ammonium carbonate.

The *acid salt*, $NH_4C_2H_3O_2.C_2H_4O_2$, is obtained as a crystalline sublimate by heating powdered sal-ammoniac with potassium or calcium acetate, ammonia being given off at the same time; also as a radiated crystalline mass by evaporating the aqueous solution of the neutral salt.

The acetates of *barium, strontium*, and *calcium* are very soluble, and can be procured in crystals; *magnesium acetate* crystallises with difficulty.

ALUMINIUM ACETATES.—The neutral salt, $Al_2(C_2H_3O_2)_6$ is very soluble in water, and dries up in the vacuum of the air-pump to a gummy mass without trace of crystallisation. If foreign salts are present, the solution of the acetate becomes turbid on heating, from the separation of a basic compound, which redissolves as the liquid cools. Aluminium acetate is much employed in calico printing: it is prepared by mixing solutions of lead acetate and alum, and filtering from the insoluble lead sulphate. The liquid is thickened with gum or other suitable material, and with it the design is impressed upon the cloth by a wood-block, or by other means. Exposure to a moderate degree of heat drives off the acetic acid, and leaves the alumina in a state capable of entering into combination with the dye-stuff.

Some very interesting researches on aluminium acetate have been published by the late Mr Walter Crum.* The solution obtained by decomposing aluminium sulphate, $Al_2(SO_4)_3$, with lead acetate, may be supposed to contain neutral aluminium acetate, $(Al_2)(C_2H_3O_2)_6$ or $Al_2O_3.3C_4H_6O_3$. This salt cannot, however, be obtained in the dry state. If the solution be rapidly evaporated at low temperatures, by being spread in thin layers on glass or porcelain, a basic *soluble* acetate is obtained, having the composition $Al_2O_3.2C_4H_6O_3 + 4$ aq.; but if the solution be left to stand in the cold, or submitted to the action of heat, *insoluble* basic salts are precipitated, differing in composition from the former by containing in the first case five, and in the second, two molecules of water instead of four.

The soluble aluminium acetate, when exposed in a dilute solution to the temperature of boiling water for several days, undergoes a very remarkable change, the whole, or nearly the whole, of the acetic acid being expelled by the action of heat, and a peculiar soluble modification of alumina (already described under ALUMINIUM, (i. 391), remaining in solution.

Manganese acetate forms colourless, rhombic, prismatic crystals, permanent in the air. *Ferrous acetate* crystallises in small, greenish-white needles, very prone to oxidation; both salts dissolve freely in water. *Ferric acetate* is a dark brownish red, uncrystallisable liquid, of powerful astringent taste. *Cobalt acetate* forms a violet-coloured, crystalline, deliquescent mass. The *nickel salt* separates in green crystals, which dissolve in 6 parts of water.

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* Chem. Soc. Quar. Jour. vi. 216.

LEAD ACETATES.—The *normal salt*, $Pb(C_2H_3O_2)_2 + 3aq.$, is prepared on a large scale by dissolving litharge in acetic acid; it may be obtained in colourless, transparent, prismatic crystals, but is generally met with in commerce as a confusedly crystalline mass, somewhat resembling loaf-sugar. From this circumstance and from its sweet taste, it is often called *sugar of lead.* The crystals are soluble in about 1¼ parts of cold water, effloresce in dry air, and melt when gently heated in their water of crystallisation; this water is easily driven off, and the anhydrous salt obtained, which melts, and afterwards decomposes, at a high temperature. Acetate of lead is soluble in alcohol. The aqueous solution has an intensely sweet, and at the same time, astringent taste, and is not precipitated by ammonia. It is an article of great value to the chemist.

Basic Acetates (Subacetates) of Lead.—A *sesquibasic acetate*, $2Pb(C_2H_3O_2)_2.PbO$, is produced when the neutral anhydrous salt is so far decomposed by heat as to become converted into a porous white mass, decomposible only at a much higher temperature. It is soluble in water, and separates from the solution evaporated to a syrupy consistence in the form of crystalline scales. A *triplumbic acetate*, $Pb(C_2H_3O_2)_2.2PbO$, is obtained by digesting at a moderate heat, 7 parts of finely powdered litharge, 6 parts of lead acetate, and 30 parts of water; or, by mixing a cold saturated solution of neutral lead acetate with a fifth of its volume of caustic ammonia, and leaving the whole for some time in a covered vessel. The salt separates in minute needles containing one molecule of water. The solution of basic acetate prepared by the first method is known in pharmacy under the name of *Goulard water.* There is also a *sexplumbic acetate*, $Pb(C_2H_3O_2)_2.5PbO$, formed by adding a great excess of ammonia to a solution of normal lead acetate, or by digesting the normal salt with a large quantity of oxide. It is a white, slightly crystalline substance, insoluble in cold, and but little soluble in boiling water. The solutions of the basic lead acetates have a strong alkaline reaction, and absorb carbonic acid with the greatest avidity, becoming turbid from precipitation of basic carbonate.

CUPRIC ACETATES.—The *normal acetate*, $Cu(C_2H_3O_2)_2+aq.$, is prepared by dissolving *verdigris* in hot acetic acid, and leaving the filtered solution to cool. It forms beautiful dark green crystals, which dissolve in 14 parts of cold and 5 parts of boiling water, and are also soluble in alcohol. A solution of this salt, mixed with sugar and heated, yields cupric oxide in the form of minute red octohedral crystals: the residual copper solution is not precipitated by an alkali. Cupric acetate yields, by destructive distillation, strong acetic acid containing acetone and contaminated with copper. The salt is sometimes called *distilled verdigris,* and is used as a pigment.

Basic Cupric Acetates.—Common verdigris, made by exposing plates of copper to the air for several weeks, in contact with acetic acid or the marc of grapes, is a mixture of several basic cupric acetates which have a green or blue colour. One of these, $2Cu(C_2H_3O_2)_2.CuO+6$ aq., is obtained by digesting the powdered verdigris in warm water, and leaving the soluble part to spontaneous evaporation. It forms a blue, crystalline mass, but little soluble in cold water. When boiled, it deposits a brown powder, which is a subsalt with large excess of base. The green insoluble residue of the verdigris contains $Cu(C_2H_3O_2)_2.2CuO+3$ aq.; it may be formed by digesting normal cupric acetate with the hydrated oxide. By boiling with water it is resolved into normal acetate and the brown basic salt.

SILVER ACETATE, $AgC_2H_3O_2$, is obtained by mixing potassium acetate with silver nitrate, and washing the precipitate with cold water to remove the potassium nitrate. It crystallises from a warm solution in small colourless needles, which have but little solubility in the cold.

Mercurous acetate forms small scaly crystals, which are as feebly soluble as those of acetate of silver. *Mercuric acetate* dissolves with facility.

METHYL ACETATE, $CH_3.C_2H_3O_2$, occurs in crude wood-spirit. It is prepared by distilling 2 parts of methyl alcohol with 1 part of glacial acetic acid and 1 part of sulphuric acid, or 1 part of methyl alcohol with 1 part of potassium acetate and 2 parts of sulphuric acid. When purified by rectification over calcium chloride and quick-lime, it forms a colourless fragrant liquid, of sp. gr. 0·9562 at 0°, boiling at 55° or 56°. It dissolves in water, and mixes in all proportions with alcohol and ether.

ETHYL ACETATE, $C_2H_5.C_2H_3O_2$, may be prepared by heating together in a retort, 3 parts of potassium acetate, 3 parts of strong alcohol, and 2 parts of oil of vitriol. The distilled product is mixed with water, to separate the alcohol, digested first with a little chalk, and afterwards with fused calcium chloride, and, lastly, rectified. The pure ether is an exceedingly fragrant limpid liquid, having a density of 0·9105 at 0°, 0·9068 at 15°, and boiling at 77°. Alkalis decompose it in the manner already mentioned (p. 273). When treated with ammonia, it yields *acetamide*, $NH_2C_2H_3O$.

On the reaction of ethyl acetate and homologous ethers with sodium and the iodides of alcohol-radicles, see p. 271; also CARBOKETONIC ACIDS.

AMYL ACETATE, $C_5H_{11}.C_2H_3O_2$, prepared in a similar manner from ordinary amyl alcohol, boils at 140°. It possesses in a remarkable manner the odour of the Jargonelle pear, and is manufactured on a large scale for flavouring liquors and confectionery.

ETHENE ACETATES.—These compounds may be derived from ethene alcohol (glycol) by substitution of one or two equivalents of acetyl for hydrogen. The *monacetate*, $(C_2H_4)\left\{\begin{matrix}OH\\OC_2H_3O\end{matrix}\right.$, is produced by heating ethene dibromide with an alcoholic solution of potassium acetate. The product is distilled, the portion coming over at 182° being kept separate. It is a colourless, oily liquid, miscible in every proportion with water or alcohol. Hydrochloric acid gas passed into ethene monacetate converts it into ethene acetochloride, or glycolic chloracetin, $C_2H_4\left\{\begin{matrix}Cl\\OC_2H_3O\end{matrix}\right.$, which is precipitated, on addition of water, as an oily liquid boiling at 145°. Treatment with potash decomposes it into ethene oxide, potassium acetate, and potassium chloride.

Ethene diacetate, $C_2H_4\left\{\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix}\right.$, is prepared by digesting a mixture of ethene dibromide, silver acetate, and glacial acetic acid in the water-bath, and exhausting the digested mass with ether. On distilling the ethereal solution, the ether first passes over, then the acetic acid, and lastly, when the temperature has reached 187°, ethene diacetate. It is a colourless, neutral liquid, of sp. gr. 1·128 at 0°, boiling at 186°, soluble in 7 parts of water and in every proportion in alcohol and ether. By distillation with potash it yields ethene alcohol, or glycol, $C_2H_4(HO)_2$.

PROPENYL OR GLYCERYL ACETATES; ACETINS.—These ethers are derived from propenyl alcohol (glycerin) by substitution of 1, 2, or 3 equivalents of acetyl for hydrogen. The formula of glycerin being $(C_3H_5)(OH)_3$, those of the three acetins are:

Monoacetin, ...	$(C_3H_5)(OH)_2(OC_2H_3O)$
Diacetin, ...	$(C_3H_5)(OH)(OC_2H_3O)_2$
Triacetin, ...	$(C_3H_5)(OC_2H_3O)_3$.

They are oily liquids, produced by heating glycerin and acetic acid together, in various proportions, in sealed tubes.

ACETIC CHLORIDE OR ACETYL CHLORIDE, C_2H_3OCl.—This compound, which has the constitution of acetic acid with chlorine substituted for hydroxyl, is produced, as already observed (p. 273), by the action of phosphorus trichloride, pentachloride, or oxychloride on glacial acetic acid. The product heated with water and dilute soda-solution, to remove phosphorus oxychloride and hydrochloric acid, and then rectified, yields acetic chloride as a colourless liquid, having a suffocating odour, and emitting dense fumes of hydrochloric acid in contact with the air. It has a density of 1·1305 at 0°, boils at 55°, and is decomposed by water and alkaline solutions, yielding hydrochloric and acetic acids.

ACETIC OXIDE or ANHYDRIDE, $C_4H_6O_3 = (C_2H_3O)_2O$, sometimes called *Anhydrous Acetic acid.*—This compound is obtained:

1. By the action of acetyl chloride on potassium or sodium acetate:

$$C_2H_3O(ONa) \ + \ C_2H_3OCl \ = \ NaCl \ + \ (C_2H_3O)_2O.$$

2. By heating sodium acetate with benzoyl chloride, C_7H_5OCl, whereby benzo-acetic oxide $(C_2H_3O)(C_7H_5O)O$, is formed in the first instance, and subsequently resolved into acetic and benzoic oxides, the former distilling over, while the latter remains:

$$C_2H_3O(ONa) \ + \ C_7H_5OCl \ = \ NaCl \ + \ C_2H_3O.O.C_7H_5O$$

and:

$$2(C_2H_3O.O.C_7H_5O) \ = \ (C_2H_3O)_2O \ + \ (C_7H_5O)_2O.$$

Acetic oxide is a heavy oil which boils at 121°, and dissolves slowly in water, being gradually converted into acetic acid:

$$(C_2H_3O)_2O \ + \ H_2O \ = \ 2C_2H_3O(OH).$$

Acetyl Peroxide $(C_2H_3O)_2O_2$, obtained by adding barium dioxide to an ethereal solution of acetyl monoxide, is a viscid liquid, which explodes with violence when heated, and acts as a powerful oxidising agent.

Acids derived from Acetic Acid by Substitution.

Chloracetic Acids.—The three acids, C_2H_3ClO, $C_2H_2Cl_2O_2$, and $C_2HCl_3O_2$, are produced by the action of chlorine on acetic acid in sunshine; the second, however, is formed in small quantity only, the first or the third being produced in greatest abundance according as the acetic acid or the chlorine is in excess.

Monochloracetic acid, $CH_2Cl.COOH$, is produced, according to R. Hoffmann, by the action of chlorine on boiling glacial acetic acid in sunshine. Dr. H. Müller finds that the formation of monochloracetic acid is facilitated by dissolving a little iodine in the hydrated acetic acid, and passing a stream of chlorine through the boiling solution. On submitting the products of this reaction to repeated distillation, monochloracetic acid is obtained as a liquid, boiling at 186°, and solidifying to a crystalline mass, which melts at 62°, and dissolves easily in water. Heated with potash, it is converted into potassium glycollate, $KC_2H_3O_3$ (p. 275):

$$C_2H_3ClO_2 \ + \ 2KHO \ = \ KCl \ + \ KC_2H_3O_3 \ + \ H_2O.$$

Dichloracetic acid, $CHCl_2.COOH$, is produced, together with the preceding compound, by the action of chlorine and iodine on boiling acetic acid, and is found in the portion of the product which boils above 188°. According to Maumené, it may be obtained by exposing monochloracetic acid in flasks to the action of dry chlorine

(5 atoms of chlorine to 3 molecules of chloracetic acid) for twenty-four hours, warming the product to expel hydrochloric acid, and then distilling. It is a liquid having a specific gravity of 1·5216 at 15°, and boiling at 190–191°. According to Müller, it remains liquid when cooled; but according to Maumené, it crystallises in rhombohedral plates. It forms a soluble silver salt, $AgC_2HCl_2O_2$, which is decomposed when its solution is heated with silver oxide to 75° or 80°, giving off a mixture of carbon monoxide and dioxide:

$$2AgC_2HCl_2O_2 + 3Ag_2O = 2CO + 2CO_2 + 4AgCl + 2Ag_2 + H_2O.$$

Trichloracetic acid, $CCl_3.COOH$. — Discovered by Dumas. When a small quantity of crystallisable acetic acid is introduced into a bottle of dry chlorine gas, and the whole exposed to the direct solar rays for several hours, the interior of the vessel is found coated with a white crystalline substance, which is a mixture of trichloracetic acid with a small quantity of oxalic acid.

Trichloracetic acid may also be produced synthetically, viz., by the action of chlorine and water on carbon dichloride, C_2Cl_4, this compound first taking up 2 atoms of chlorine and forming carbon trichloride, C_2Cl_6, and the latter being converted by the water into hydrochloric and trichloracetic acids:

$$C_2Cl_6 + 2H_2O = 3HCl + C_2HCl_3O_2.$$

Trichloracetic acid is a colourless and extremely deliquescent substance: it has a faint odour, and sharp caustic taste, bleaching the tongue and destroying the skin; the solution is powerfully acid. It melts at 52°, and boils without decomposition at 195–200°, giving off a very irritating vapour. The density of the fused acid is 1·617.

Potassium trichloracetate, $2KC_2Cl_3O_2.aq.$, crystallises in fibrous silky needles, permanent in the air. The *ammonium-salt*, $2(NH_4)C_2Cl_3O + 5aq.$, is also crystallisable and neutral. The *silver-salt*, $AgC_2Cl_3O_2$, is soluble, and crystallises in small, greyish scales, easily altered by light.

Trichloracetic acid boiled with excess of ammonia yields ammonium carbonate and chloroform:

$$C_2HCl_3O_2 + 2NH_3 + H_2O = (NH_4)_2CO_3 + CHCl_3.$$

With caustic potash, it yields a smaller quantity of chloroform, together with potassium chloride, carbonate, and formate. The chloride and formate are secondary products of the reaction of the alkali upon the chloroform.

Nascent hydrogen reduces trichloracetic to acetic acid. When potassium or sodium amalgam is put into a strong aqueous solution of trichloracetic acid, the temperature of the liquid rises, without disengagement of gas, and the solution is found to contain acetate and chloride of potassium or sodium, together with caustic alkali.

Bromacetic Acids.—The *mono-* and *di-*brominated acids are formed by heating acetic acid or ethyl acetate with bromine in sealed tubes to 180°. $CH_2Br.CO_2H$ crystallises in deliquescent rhombohedrons, and boils at 208°. Its *ethylic ether* is a liquid boiling at 159°. The acid is converted by ammonia into glycerin (p. 275). $C_2HBr_2.CO_2H$ is a crystalline mass melting at 45°–50°, and boiling at 232°–234°. Heated with moist silver oxide it yields bromo glycollic acid, $C_2H_3BrO_3$. Its ethylic ether boils at 192°–195°. *Tribromacetic Acid*, $C_2Br_3.CO_2H$ is produced by the action of water on tribromacetyl bromide, $CBr_3.COCl$, and by oxidation of bromal, $CBr_3.COH$, with nitric acid. It forms deliquescent crystals, melts at 130° and boils at 245°.

Iodacetic Acids, *mono-* and *di-*, are obtained by heating the chlorinated or brominated acids with potassium iodide; also by heating acetic anhydride with iodine and iodic acid. $C_2H_2I.CO_2H$ crystallises in colourless laminæ, melting, with partial decomposition at 82°; reconverted into acetic acid by boiling with HI. Its ethylic ether boils at 178°–180°.

Cyanacetic Acid, $C_3H_3NO_2 = CH_2(CN).CO_2H$, formed by heating monochloracetic acid with potassium cyanide and water, is a crystalline mass melting at about 80°, and decomposed at 165° into CO and acetonitril, $CH_3.CN$.

Thiacetic Acid, C_2H_4OS, or $CH_3.COSH$.—This acid, discovered by Kekulé, is formed by the action of phosphorus pentasulphide on glacial acetic acid:

$$5C_2H_3O(OH) + P_2S_5 = P_2O_5 = 5C_2H_3O(SH).$$

Thiacetic acid is a colourless liquid, boiling at 93°; it smells like acetic acid and hydrogen sulphide. With solution of lead acetate, it forms a crystalline precipitate containing $(C_2H_3OS)_2Pb$.

Propionic Acid, $C_3H_6O_2 = C_3H_5O(OH) = C_2H_5.CO.OH$.—This acid is produced: 1. As a potassium-salt, by the combination of carbon dioxide with potassium-ethyl: $CO_2 + C_2H_5K = CO(C_2H_5)OK$. 2. By the action of acids or alkalis on ethyl cyanide (p. 270). 3. By the simultaneous action of water and carbonyl chloride on ethane (p. 270). 4. By the oxidation of normal propyl alcohol (p. 143), and of propionic aldehyde, C_3H_6O. 5. Together with acetic acid, by oxidising propione, $C_5H_{10}O$, with dilute chromic acid. This is the process by which it was first obtained. 6. From lactic acid and from glyceric acid by the action of hydriodic acid:

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} + 2HI = C_3H_6O_2 + H_2O + I_2.$$

$$\underset{\text{Glyceric acid.}}{C_3H_6O_4} + 4HI = C_3H_6O_2 + 2H_2O + 2I_2.$$

7. Together with several other products, in the fermentation of glycerin, and likewise of sugar, by the action of putrid cheese in presence of calcium carbonate.

Propionic acid is usually prepared by the second of the above-mentioned processes. Ethyl cyanide is added by drops to a moderately strong solution of potash heated in a tubulated retort, the distillate being repeatedly poured back as long as it smells o ethyl cyanide. The residue in the retort, consisting of potassium propionate, is then evaporated down to dryness, and distilled with syrupy phosphoric acid.

Propionic acid is a colourless liquid, having a specific gravity of 0·992 at 18°, and boiling at 140°. It is soluble in water, and when the water is quite saturated with it, the excess of acid floats on the surface in the form of an oil.

The propionates are soluble in water. The *barium salt*, $(C_3H_5O_2)_2Ba + H_2O$, crystallises in rhombic prisms, and yields propione by dry distillation. The *silver salt*, $C_3H_5O_2Ag$, crystallises in slender needles.

Substitution-products.—The replacement of one hydrogen-atom in propionic acid by a haloïd element, X, yields two series of substitution-products distinguished as α and β; viz:

$$\underset{\alpha.}{CH_3—CHX—CO_2H} \qquad \underset{\beta.}{CH_2X—CH_2—CO_2H}$$

Chloropropionic acids, $C_3H_5ClO_2$.—The α-acid is formed by decomposing lactyl chloride with water:

$$CH_3—CHCl—CO_2Cl + H_2O = HCl + CH_3—CHCl—CO_2H.$$

It is a thick liquid of specific gravity 1·28, and boiling at 186°. When heated with moist silver oxide, it is converted into α-lactic acid, $CH_3—CHOH—CO_2H$. Its ethylic ether, obtained by heating lactyl chloride with alcohol, boils at 144°.

The β-acid is produced by the action of chlorine-water on β-iodopropionic acid, and by addition of hydrogen chloride to acrylic acid, $C_3H_4O_2$:

$$CH_2{=}CH—CO_2H + ClH = CH_2Cl—CH_2—CO_2H.$$

It is crystalline, and melts at 40·5°. Its ethylic ether boils at about 155°

Bromopropionic acids, $C_3H_5BrO_2$.—The α-acid is obtained by the action of bromine on propionic acid, and by heating α-lactic acid (ordinary lactic acid) with hydrobromic acid, is a liquid which solidifies at −17°, and boils at 202°. Its ethylic ether smells like camphor, and boils at 190°. Alcoholic ammonia converts it into α-amidopropionic acid or alanine, $C_3H_5(NH_2)O_2$ (see AMIDES). The β-acid, formed by the action of bromine-water on β-iodopropionic acid, and by addition of hydrobromic acid to acrylic acid, is crystalline, and melts at 61·5°.

α-Iodopropionic acid, $C_3H_5IO_2$, is a thick oil, obtained by the action of phosphorus iodide on α-lactic acid.

The β-acid is obtained by the action of phosphorus iodide and a small quantity of water on glyceric acid:

$$CH_2OH.CHOH.CO_2H + 3HI = CH_2I.CH_2.CO_2H + 2H_2O + I_2;$$

also by addition of hydriodic acid to acrylic acid. It crystallises in large colourless six-sided plates, having a peculiar odour, and melting at 82°: easily soluble in hot water. By heating with strong hydriodic acid, it is reduced to propionic acid.

The di-substitution products of propionic acid admit of three modifications, viz.:

$$\underset{\alpha.}{CH_3—CX_2—CO_2H} \quad \underset{\beta.}{CH_2X—CHX—CO_2H} \quad \underset{\gamma.}{CHX_2—CH_2—CO_2H}$$

The first two modifications of the chlorine and bromine derivatives are known.

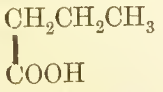
α-Dibromopropionic acid, $CH_3—CBr_2—CO_2H$, obtained by direct bromination of propionic or α-bromopropionic acid, melts at 61°, and boils at 220°. Its ethylic ether boils at 190°.

β-Dibromopropionic acid, $CH_2Br—CHBr—CO_2H$, obtained by oxidation of dibromopropyl alcohol, $C_3H_6Br_2O$ (formed by addition of bromine to allyl alcohol), and by addition of Br_2 to acrylic acid, $CH_2{=}CH—CO_2H$, forms crystals easily soluble in water, melting at 65°, decomposed by distillation. The ethylic ether boils at 212°.

α-Dichloropropionic acid, $CH_3—CCl_2—CO_2H$. The ethylic ether of this acid is formed by the action of alcohol on the chloride, $CH_3—CO—COCl$, produced by the action of phosphorus pentachloride on pyroracemic acid, $CH_3—CO—COOH$. It is a colourless liquid, having a pleasant odour of apples, a specific gravity of 1·2493 at 0°, and boiling at 160°. Heated with water to 150°, it is converted into pyroracemic acid.

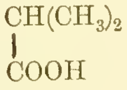
β-Dichloropropionic acid, $CH_2Cl—CHCl—CO_2H$, is formed by the action of water on the chloride obtained by heating glyceric acid with phosphorus pentachloride.

Butyric acid, $C_4H_8O_2 = C_3H_7.CO_2H$.—Of this acid there are two modifications, viz.:



$$\begin{array}{l} CH_2CH_2CH_3 \\ | \\ COOH \end{array}$$

Normal butyric.



$$\begin{array}{l} CH(CH_3)_2 \\ | \\ COOH \end{array}$$

Isobutyric.

Normal Butyric acid, also called *Fermentation Butyric*, *Propyl-formic*, and *Ethyl-acetic acid*, occurs, either free or combined with bases, in tamarinds and a few other plants, in certain beetles, in flesh-juice, in human perspiration, and in various kinds of decomposing vegetable and animal matter. As a glyceride, it occurs in various animal and vegetable fats, especially in the butter of cows' and goats' milk; as a hexyl ether in the oil of *Heracleum giganteum*, and as an octyl ether in oil of parsnep (*Pastinaca sativa*). It is formed by the oxidation of normal butyl alcohol; by the action of nascent hydrogen on crotonic acid, $CH_3—CH=CH—CO_2H$; by heating normal propyl cyanide (butyronitril) with alkalis or acids; by the action of sodium and ethyl iodide on ethyl acetate (p. 271); and by the fermentation of sugar in contact with putrid cheese.

This last reaction affords the most convenient method of preparing the acid. The fermentation takes place, however, only in neutral liquids, so that it is necessary to add chalk, in order to neutralise the acid as fast as it is formed. The sugar is first converted into lactic and afterwards into butyric acid. The following proportions give a good result:—6 pounds of cane-sugar and half an ounce of tartaric acid are dissolved in 26 pounds of boiling water, and the solution is left for some time to allow the cane-sugar to pass into grape-sugar. To this solution about 4 ounces of decayed cheese diffused in 8 pounds of sour skim-milk, together with 3 pounds of chalk, are added, and the whole is kept for some weeks at a temperature of 30°–35°. The mixture is frequently stirred, and generally solidifies in ten or twelve days to a thick mass of calcium lactate. This, however, soon disappears, the mixture becoming liquid, and the lactate being converted into butyrate, with simultaneous evolution of carbon dioxide and hydrogen:

$$2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2.$$

When fermentation is completed, a solution of 8 pounds of crystallised sodium carbonate is added, and the filtered liquid, after concentration, is decomposed by sulphuric acid. Butyric acid then separates as an oily layer, which is dried over calcium chloride and rectified.

Butyric acid is a viscid liquid having a rancid odour, solidifying at $-12°$, and boiling at 163°. Specific gravity 0·958 at 14°. It dissolves easily in water and in alcohol, and separates from the aqueous solution on addition of salts.

The metallic butyrates are for the most part soluble in water and crystallisable. The *calcium salt*, $(C_4H_7O_2)Ca+H_2O$, forms shining laminæ, and is *more soluble in cold than in hot water*. The *silver salt*, $C_4H_7O_2Ag$, crystallises in shining laminæ, soluble in 400 parts of water at 14°.

Ethyl Butyrate, $C_4H_7O_2.C_2H_5$, is a liquid having a pleasant fruity odour, and boiling at 119°.

The butyrates unite with acetates, forming double salts, which react like salts of butyracetic acid, $C_4H_8O_2.C_2H_4O_2$, isomeric with propionic acid. This acid, obtained in the free state by the fermentation of calcium tartrate, differs from propionic acid in being resolved by distillation into butyric and acetic acids.

A *monochlorobutyric acid*, $C_4H_7ClO_2$, crystallising in slender needles and melting at 99°, is formed by the action of chlorine on butyric acid in presence of iodine.

Out of five possible *monobromobutyric acids*, two, viz.,

$$CH_3—CH_2—CHBr—CO_2H \qquad CH_3—CHBr—CH_2—CO_2H$$

$$\alpha, \qquad \beta,$$

are formed by the addition of HBr to crotonic acid. The action of bromine on butyric acid yields chiefly the α-acid, the ethylic ether of which boils at 170°–172°. The two acids are converted by boiling with potash-solution or moist silver oxide into the corresponding oxybutyric acids, $C_4H_8O_3$.

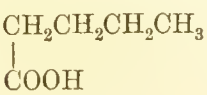
A *dibromobutyric acid*, $C_4H_6Br_2O_2$, melting at 45°–48°, is formed by further bromination of butyric acid.

Isobutyric Acid, $HC(CH_3)_2—CO_2H$, also called *Isopropyl-formic* and *Dimethyl-acetic acid*, occurs in the free state in St. John's bread, the fruit of *Ceratonia siliqua*, and as an octylic ether in parsnep oil. It is produced by oxidation of isobutyl alcohol, by the action of alkalis or acids on pseudopropyl cyanide; and by the action of sodium and methyl iodide on ethyl acetate (p. 271).

This acid is very much like normal butyric acid, but has a less disagreeable odour, and is not miscible with water. It has a specific gravity of 0·960 at 0°, and boils at 154°. Its *calcium salt*, $(C_4H_7O_2)_2Ca + 5H_2O$, crystallises in monoclinic prisms, *much more soluble in hot water than in cold.* The silver salt dissolves in 110 parts of water at 16°. The *ethylic ether*, $C_4H_7O_2.C_2H_5$, has a specific gravity of 0·8893 at 0°, and boils at 110°.

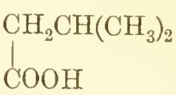
Bromisobutyric acid, $(CH_3)_2CBr.CO_2H$, formed by heating isobutyric acid with bromine to 140°, forms crystals melting at 45°, and is partly decomposed by boiling. Its ethylic ether has a specific gravity of 1·328 at 0°, and boils at 158°–159°. By heating with moist silver-oxide or baryta-water, this acid is converted into the corresponding oxyisobutyric acid.

Pentoic or **Valeric Acids**, $C_5H_{10}O_2 = C_5H_9O(OH)$.—These acids admit of four metameric modifications, namely,



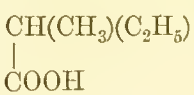
$$\begin{array}{l} CH_2CH_2CH_2CH_3 \\ | \\ COOH \end{array}$$

Propyl-acetic.



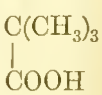
$$\begin{array}{l} CH_2CH(CH_3)_2 \\ | \\ COOH \end{array}$$

Isopropyl-acetic.



$$\begin{array}{l} CH(CH_3)(C_2H_5) \\ | \\ COOH \end{array}$$

Methyl-ethyl-acetic.



$$\begin{array}{l} C(CH_3)_3 \\ | \\ COOH \end{array}$$

Trimethyl-acetic.

The first and second are obtained by oxidation of normal pentylic and isopentylic or amylic alcohol (p. 148) respectively; the third is not known; the fourth is produced from tertiary butylic alcohol or trimethyl-carbinol.

Propyl-acetic or **Normal Valeric Acid**, $C_4H_9.COOH$, is an oily liquid, smelling like butyric acid, having a sp. gr. of 0·9577 at 0°, and boiling at 185°.

Isopentoic, Isopropyl-acetic or **Isovaleric Acid** (ordinary valeric acid), occurs in valerian root, in angelica root, in the berries of the guelder rose (*Viburnum Opulus*), and probably in many other plants. It is produced by the oxidation of ordinary amyl alcohol, either by absorption of atmospheric oxygen under the influence of platinum black, or by treatment with aqueous chromic acid, or by heating it with a mixture of caustic potash and quicklime, the reaction, in this last case, being attended with evolution of hydrogen :

$$C_5H_{12}O + KOH = C_5H_9O_2K + 2H_2.$$

The potassium salt, distilled with sulphuric acid, yields the acid.

The most advantageous mode of preparing isovaleric acid, is to oxidise amyl alcohol with a mixture of sulphuric acid and potassium dichromate. 4 parts of the dichromate in powder, 6 parts of oil of vitriol, and 8 parts of water are mixed in a capacious retort, and 1 part of amyl alcohol is added by small portions, with strong agitation, the retort being plunged into cold water to moderate the violence of the reaction. When the change appears complete, the deep-green liquid is distilled nearly to dryness, the product mixed with excess of caustic potash, and the aqueous solution separated mechanically from a pungent, colourless, oily liquid which floats upon it, consisting of amyl valerate. The alkaline solution is then evaporated to a small bulk, and decomposed by dilute sulphuric acid in excess. The greater part of the valeric acid then separates as an oily liquid lighter than water : this is a hydrate consisting of $C_5H_{10}O_2.H_2O$. When distilled alone, it undergoes decomposition : water, with a little of the acid, first appears, and eventually the pure acid, $C_5H_{10}O_2$, in the form of a thin, mobile, colourless oil, having the persistent and characteristic odour of valerian root. It has a sharp and acid taste, reddens litmus strongly, bleaches the tongue, and burns when inflamed with a bright, yet smoky light. Isovaleric acid has a density of 0·947 at 0° and boils at 175°. Placed in contact with water, it absorbs a certain quantity, and is itself to a certain extent dissolved.

Isovaleric acid is active or inactive to polarised light, accordingly as it has been prepared from active or inactive amyl alcohol. That which has been prepared from the active alcohol produces a right-handed rotation of 43° in a tube 50 centimeters long. The difference between these two acids, like that of the alcohols from which they are derived, is probably due to difference rather of molecular than of atomic arrangement (p. 38).

The metallic isovalerates are greasy to the touch and mostly crystallise with difficulty. Small fragments of them thrown on water, rotate on the surface as they dissolve. The *barium salt* $(C_5H_9O_2)_2Ba + H_2O$ usually crystallises in thin laminæ, soluble in two parts of cold, and in a smaller quantity of warm water. The *zinc salt* $(C_5H_9O_2)_2Zn$ forms shining scales. The *silver salt* $C_5H_9O_2Ag$ forms scales soluble in 540 parts of water at 20°. A solution of potassium valerate, subjected to electrolysis, yields dibutyl, C_8H_{18} (p. 273).

Ethyl isovalerate, $C_5H_9O_2.C_2H_5$, is obtained by passing hydrochloric acid gas into an alchoholic solution of valeric acid. Ammonia converts it into valeramide, $C_5H_9ONH_2$. It is decomposed by sodium in the same manner as ethyl acetate (p. 271), yielding sodium ethylate and the sodium salt of an acid, $C_{15}H_{28}O_3$:

$$4Na + 3(C_2H_5.C_5H_9O_2) = 3C_2H_5ONa + C_{15}H_{27}O_3Na.$$

CHLOROVALERIC ACIDS.—*Trichlorisovaleric acid*, $C_5H_7Cl_3O_2$, obtained by the prolonged action of chlorine on isovaleric acid in the dark, aided towards the end of the process by a gentle heat, is an oily liquid, becoming very viscid at 18°, perfectly mobile at 30°. In contact with water it forms a very viscid hydrate, which sinks to the bottom. It dissolves in aqueous alkalis, and is precipitated by acids in its original state.

Tetrachlorisovaleric acid, $C_5H_6Cl_4O_2$, is the ultimate product of the action of chlorine on the preceding compound, aided by exposure to the sun. It is a semifluid, colourless oil, destitute of odour, of powerful pungent taste, and heavier than water. It can neither be solidified by cold, nor distilled without decomposition. In contact with water, it forms a hydrate containing $C_5H_6Cl_4O_2.H_2O$, which is slightly soluble in water, easily soluble in alcohol and ether.

Neopentoic or **Trimethyl-acetic Acid**, $(CH_3)_3C.COOH$, is obtained from tertiary butyl iodide, $(CH_3)_3CI$, by converting this ether into the cyanide, and distilling the latter with potash; also by oxidation of pinacolin, $CH_3—CO—C(CH_3)_3$. It is a laminar crystalline mass, melting at 34°–35°, and boiling at 161°. It smells like acetic acid, and dissolves in 40 parts of water at 20°.

The *barium salt*, $(C_5H_9O_2)_2Ba + 5H_2O$, and the *calcium salt*, $Ca(C_5H_9O_2)_2 + 4H_2O$, crystallise in needles or prisms.

The *silver salt*, $C_5H_9O_2Ag$, is obtained by precipitation in glittering spangles. The *ethylic ether*, $C_5H_9O_2.C_2H_5$, has a specific gravity of 0·8772 at 0°, and boils at 118·5°

Hexoic or **Caproic acids**, $C_6H_{12}O_2 = C_5H_{11}.CO_2H$.—There are eight possible forms of these acids, analogous to the eight pentyl alcohols, and five of them are known, viz.:

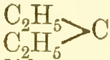
1. **Normal Caproic** or **Pentyl-formic Acid**, $CH_3(CH_2)_4.CO_2H$. —This acid is formed synthetically by heating normal pentyl cyanide, $CH_3(CH_2)_4.CN$, with strong potash-solution. It is also produced, together with other acids of the fatty series, by the oxidation of albuminous substances, and of fatty acids of higher atomic weight. It occurs in the free state in perspiration, as an octylic ether, $C_6H_{11}O_2.C_8H_{17}$, in the volatile oil of cow-parsnep (p. 157), as a glyceride in the butter of cows' milk, and abundantly in cocoa-nut oil. From this oil it may be prepared by saponifying with strong soda-ley, and distilling the soap with dilute sulphuric acid. The distillate contains caproic and caprylic acids, and, when neutralised

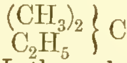
with baryta and evaporated, yields crystals of barium caprylate, and afterwards verucose crystals of the caproate, which, when decomposed by sulphuric acid, yield caproic acid.

Normal caproic acid is a clear mobile oil, having a somewhat sudorific and pungent odour, a specific gravity of 0·945 at 0°, 0·895 at 99°, and boiling at 205°. The barium salt, $(C_6H_{11}O_2)_2Ba + 3H_2O$, dissolves in 6–7 parts of water at 23°. The *ethylic ether*, $C_6H_{11}.O_2C_2H_5$., has a fruity smell, and boils at 167°.

Isocaproic or **Isopentyl-formic acid,** $CH(CH_3)_2.CH_2.CH_2.CO_2H$, prepared from isopentyl (amyl) cyanide, has a specific gravity of 0·931 at 0°, and boils at 199°–200°. Its odour resembles that of the normal acid, but is stronger and more disagreeable. The *calcium salt*, $(C_6H_{11}O_2)_2Ca + 3H_2O$, dissolves in 9 parts of water at 18°. The *ethylic ether*, $C_6H_{11}O_2.C_2H_5$, has a specific gravity of 0·887 at 0°, and boils at 160·4°.

3. **Methylisopropyl-acetic acid,** $\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}{>}CH.CO_2H$, prepared from the iodide of methyl-isopropyl carbinol (amylene hydrate, p. 151), through the medium of the cyanide, is an oil having a fruity smell. Its calcium salt crystallises in scales, and is more soluble in cold than in hot water.

4. **Diethyl-acetic acid,**  $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}CH.CO_2H$, prepared by the action of sodium and ethyl iodide on methyl acetate (p. 271), is an oil, sparingly soluble in water. Its *silver salt*, $C_6H_{11}O_2Ag$, crystallises in shining needles. The *ethylic ether*, $C_6H_{11}O_2.C_2H_5$, boils at 151°.

5. **Dimethyl-ethyl-acetic acid,**  $\left.\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\right\}C.CO_2H$, formed from tertiary butyl iodide, $(CH_3)_2(C_2H_5)CI$, through the medium of the cyanide, is a liquid which boils at 187°, and solidifies in the crystalline form at 14°. Its *barium salt*, $(C_6H_{11}O_2)_2Ba + 5H_2O$, crystallises in large laminæ.

Heptoic Acids, $C_7H_{14}O_2 = C_6H_{13}.CO_2H$. Of the 17 possible modifications of these acids, one only is accurately known, viz.:

Normal Heptoic or *Œnanthylic acid*, $CH_3(CH_2)_5.CO_2H$, which is formed by the action of boiling potash on normal hexyl cyanide, $CH_3(CH_2)_5.CN$, by the oxidation of normal heptyl alcohol, and from œnanthol or heptoic aldehyde, $C_7H_{14}O$, (p. 254), by oxidation in the air, or with nitric acid, or with chromic acid; also by oxidation of castor-oil with nitric acid.

Œnanthylic acid is a transparent colourless oil, having an unpleasant odour like that of codfish. It boils at 223°. It is insoluble in water, but soluble in alcohol and ether. When heated with baryta, it gives off hexane, C_6H_{14}, the baryta abstracting carbon dioxide: $C_7H_{14}O_2 = CO_2 + C_6H_{14}$. The potassium-salt subjected to electrolysis, yields **dihexyl**, $C_{12}H_{26}$. The *calcium salt*, $(C_7H_{13}O_2)_2Ca + H_2O$, crystallises in flattened needles, soluble in 100 parts of water at 8°. The *ethylic ether*, $C_7H_{13}O_2.C_2H_5$, has a fruity odour, a specific gravity of 0·873 at 16°, and boils at 188°.

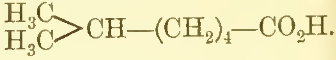
Another heptoic acid has been obtained by the action of amyl iodide on ethylic sodacetate, $CH_2Na.CO_2C_2H_5$.

Caprylic Acid, $C_8H_{16}O_2 = C_7H_{15}.CO_2H$, occurs as a glyceride in the butter of cows' milk and in cocoa-nut oil; it is also found in several kinds of fusel-oil, partly free, partly as an ethylic or amylic ether. It is best prepared by saponification of cocoa-nut oil; its barium-salt being very sparingly soluble, is easily separated from the barium-salt of caproic acid formed at the same time.

Caprylic acid has a faint but unpleasant odour, especially when warmed. It solidifies at 12°, melts at 15°, and boils at 236°–238°. When boiled with nitric acid, it is converted into nitrocaprylic acid, $C_8H_{15}(NO_2)O_2$.

Primary octyl alcohol, $C_8H_{18}O$, obtained from Heracleum oil (p. 157), yields by oxidation with chromic acid an acid, $C_8H_{16}O_2$, solidifying at 12°, melting at 16°–17°, boiling at 234°–238°, and doubtless identical with the caprylic acid of natural fats; but the primary octyl alcohol obtained from the octane of American petroleum, yields by oxidation an acid isomeric with the above, inasmuch as when floating on water, it remains liquid at 0°.

As the primary octyl alcohol of Heracleum oil is an iso-alcohol (p. 157), it follows that the caprylic acid formed from it by oxidation, and therefore also that obtained from natural fats, must be an iso-acid, viz., isoheptyl-formic acid,



$$\begin{matrix}H_3C\\H_3C\end{matrix}\!>CH-(CH_2)_4-CO_2H.$$

Pelargonic or **Nonylic Acid** $C_9H_{18}O_2 = C_8H_{17}.CO_2H$, was first obtained from the leaves of the geranium (*Pelargonium roseum*), in which it exists ready formed. It may be procured in large quantity by the action of nitric acid upon the essential oil of rue (which contains nonyl-methyl ketone $C_9H_{19}.CO.CH_3$); also, together with several other acids of the fatty series, by the action of boiling nitric acid on oleic acid. It is also formed synthetically by the action of boiling alcoholic potash on primary octyl cyanide, $C_8H_{17}.CN$, prepared from the octyl alcohol of Heracleum oil. It is a liquid having a slightly unpleasant odour, solidifying at 12 – 12·5°, and boiling at 253 – 254°.

Ethyl pelargonate, $C_9H_{17}O_2.C_2H_5$, may be easily produced by dissolving the acid in strong alcohol, and passing a current of hydrochloric acid through the solution. It is a liquid of specific gravity 0·862, and boiling at 250°. It has a powerful and most intoxicating vinous odour.

The aroma possessed by certain wines appears to be due to the presence of the ether of pelargonic acid, which, in this case, is probably generated during fermentation. When such wines, or the residues of their fermentation, are distilled on the large scale, an oily liquid passes over towards the close of the operation, which consists, in a great measure, of the crude ether: it may be purified by agitation with solution of potassium carbonate, freed from water by a fe fragments of calcium chloride, and redistilled. The pelargonic ether obtained by this process was originally described as *œnanthic ether*, and the acid as *œnanthic acid.*

Rutic or Capric Acid, $C_{10}H_{20}O_2$.—This acid exists as a glyceride in ordinary butter and in cocoa-nut oil; it occurs also in several kinds of fusel-oil, and is formed by the oxidation of oleic acid and of oil of rue. It may be obtained pure and in tolerable quantity from the liquid which remains in the distillation of the fusel-oil of the Scotch distilleries (p. 151) after the amyl alcohol has been distilled off at 132°. This residue consists chiefly of amyl rutate, $C_{10}H_{19}O_2.C_5H_{11}$., and when distilled with potash gives off amyl alcohol and leaves potassium rutate, from which the rutic acid may be obtained by distillation with sulphuric acid.

Rutic acid is a colourless crystalline body, having a slight odour of the goat, becoming stronger when the acid is warmed. It melts at 27–30°, boils at 268–270°, is very soluble in cold alcohol and ether, insoluble in cold water, slightly soluble in boiling water, and dissolves without alteration in strong nitric acid.

The metallic rutates are mostly sparingly soluble in water. The barium salt, $(C_{10}H_{19}O_2)_2Ba$, separates from solution in boiling water in needle-shaped or large prismatic crystals which float on the water if not moistened.

Lauric Acid, $C_{12}H_{24}O_2$, occurs as a glyceride (laurostearin) in the fat of the bay-tree (*Laurus nobilis*), and in the solid fat and volatile oil of pichurim beans (*Fabæ Pichurim maj.*). It is prepared by saponifying these fats with caustic alkali, and decomposing the resulting soap with tartaric or hydrochloric acid. It likewise occurs, together with other fatty acids, or their glycerides, in cocoa-nut oil and the oils or fats of several other plants, also in spermaceti; and is separated from the mixtures of fatty acids resulting from the saponification of these substances by a complicated process of fractional precipitation with barium and magnesium salts, into the details of which we cannot enter.*

Lauric acid is insoluble in water, but dissolves easily in alcohol and ether, and crystallises from alcohol in white, silky needles, which melt at about 43°.

The laurates of the alkali-metals and of barium are soluble in water; the other salts are insoluble or sparingly soluble. The *calcium salt*, $(C_{12}H_{23}O_2)_2Ca$, is resolved by distillation into calcium carbonate and laurostearone:

$$(C_{12}H_{23}O_2)_2Ca \quad = \quad CO_3Ca \quad + \quad C_{23}H_{46}O\,.$$

Myristic Acid, $C_{14}H_{28}O_2$, occurs as a glyceride in nutmeg-butter and Otoba fat; also, together with lauric acid, in Dika bread, the fruit of *Mangifera gabonensis*, an African tree; and, together with other fatty acids, in cocoa-nut oil and spermaceti. It may be produced from crude ethal (cetyl alcohol) by heating with a mixture of potash and lime, its formation being doubtless due to the presence of methal or myristic alcohol, $C_{14}H_{30}O$, in the crude ethal (p. 160):

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* See Watts's Dictionary of Chemistry, vol. iii. p. 474.

$$C_{14}H_{30}O + KHO = C_{14}H_{27}O_2K + 2H_2.$$

Lauric acid is likewise produced by a similar process from crude ethal, doubtless because that substance also contains lethal or lauric alcohol, $C_{12}H_{26}O$.

Pure myristic acid is most easily obtained by saponification of Otoba fat (from *Myristica Otoba*). It forms white, shining crystalline laminæ, melting at 53·8°. It is quite insoluble in water and in ether, but dissolves easily in hot alcohol, and crystallises therefrom on cooling.

The myristates of the alkali-metals, $C_{14}H_{27}O_2K$, &c., are soluble in water, and not decomposed thereby (like the stearates). The other myristates are insoluble or sparingly soluble, and are obtained by precipitation.

Myristin, $(C_3H_5)(C_{14}H_{27}O_2)_3$, the glyceride of myristic acid, is obtained by pressing nutmegs between hot plates, exhausting the crude fat thus obtained with spirits of wine, and crystallising the undissolved portion from boiling ether. It is a crystalline fat having a silky lustre.

Palmitic Acid, $C_{16}H_{32}O_2$., occurs as a glyceride (tripalmitin) in many natural fats, often associated with stearin. Palm-oil, the produce of *Elais guianensis*, Chinese tallow, the produce of the tallow-tree (*Stillingia sebifera*), and Japan wax, from *Rhus succedanea*, consist mainly of tripalmitin. Palmitic acid is easily prepared by saponifying palm-oil with caustic potash, decomposing the soap with sulphuric acid, and crystallising the separated fatty acid several times from hot alcohol till it exhibits a constant melting-point. Chinese tallow may be saponified with alcoholic potash, and Japan wax by fusion with solid potassium hydrate, and the soap treated in a similar manner.

Palmitic acid exists also as cetyl palmitate (cetin), $C_{16}H_{33}.C_{16}H_{31}O_2$, in spermaceti, and as myricyl palmitate (melissin), $C_{30}H_{61}.C_{16}H_{31}O_2$, in bees'-wax. It is produced, together with acetic acid, by melting oleic acid, $C_{18}H_{34}O_2$, with potassium hydrate:

$$C_{18}H_{34}O_2 + 2KOH = C_{16}H_{31}O_2K + C_2H_3O_2K + H_2.$$

Palmitic acid is a colourless, solid body, without taste or smell, lighter than water. It is insoluble in water, but dissolves abundantly in boiling alcohol or ether. The solutions are acid, and when concentrated, solidify in a mass on cooling. When dilute they yield the acid in tufts of slender needles. It melts at 62°, and solidifies on cooling in a mass of shining nacreous laminæ. When heated in a dish it boils and evaporates without residue, and may be distilled almost without change. When gently heated in the air, it is but slightly altered, but at higher temperatures it takes fire, and burns with a bright smoky flame like other fats. It is attacked by chlorine at 100°, giving off hydrochloric acid, and forming oily substitution-products. Heated with alcohols, it forms compound ethers.

Palmitic acid forms normal or neutral salts, having the composition $MC_{16}H_{31}O_2$ for univalent, and $M''(C_{16}H_{31}O_2)_2$ for bivalent metals, and with the alkali-metals also, acid salts analogous to the acid acetates. The normal palmitates of potassium and sodium are soluble in water and alcohol ; the rest are insoluble, and are obtained by precipitating a metallic salt with an alcoholic solution of sodium or potassium palmitate.

Ethyl palmitate, $C_2H_5.C_{16}H_{31}O_2$, obtained by passing hydrochloric acid gas into a saturated alcoholic solution of palmitic acid, crystallises in prisms, and melts at 24°.

Glyceryl Palmitates or Palmitins.—There are three of these ethers—viz., *Monopalmitin*, $C_3H_5\left\{\begin{matrix}(OH)_2\\C_{16}H_{31}O_2\end{matrix}\right.$, *dipalmitin*, $C_3H_5\left\{\begin{matrix}OH\\(C_{16}H_{31}O_2)_2\end{matrix}\right.$, and *tripalmitin*, $C_3H_5(C_{16}H_{31}O_2)_3$. The first and second are obtained by heating palmitic acid with glycerin in sealed tubes ; the third by heating a mixture of 1 part of monopalmitin and 10 parts of palmitic acid to 250° for twenty-eight hours. They are all crystalline fats. Tripalmitin thus obtained melts at 46°. Natural palmitin, obtained from palm-oil and other fats, has the composition of tripalmitin, but exhibits three isomeric (or rather allotropic) modifications (like those of stearin) melting respectively at 46°, 61·7°, and 62·8°: the first appears to be identical with artificial tripalmitin.

Palm-oil comes chiefly from the coast of Africa. It has, when fresh, a deep orange-red tint, and a very agreeable odour: the colouring matter—the nature of which is unknown—is easily destroyed by exposure to light, especially at a high temperature, and also by oxidising agents. The oil melts at 27°. By cautious pressure it may be separated into fluid olein and solid palmitin, which, when purified by crystallisation from hot ether, is perfectly white. By keeping, palm-oil seems to suffer a change similar to that produced by saponification : in this state it is found to contain traces of glycerin and a considerable quantity of oleic acid, together with palmitic acid. The oil becomes harder and rancid, and its melting-point is raised at the same time.

Margaric Acid, $C_{17}H_{34}O_2$.—This name was formerly applied to an acid, intermediate between stearic and palmitic acids, supposed to be produced, together with others, by the saponification of natural fats ; but it is now restricted, for reasons to be presently mentioned, to an acid prepared by a definite reaction—viz., by the action of boiling alcoholic potash on cetyl cyanide :

$$C_{16}H_{33}CN + KOH + H_2O = NH_3 + C_{17}H_{33}O_2K.$$

The solid potassium salt thus obtained is decomposed by boiling dilute hydrochloric acid, and the separated margaric acid is purified by precipitating its ammoniacal solution with barium chloride, decomposing the precipitate with hydrochloric acid and ether, separating the ethereal solution by means of a pipette; and distilling off the ether. It forms white crystals, melting at 59·9°, and is intermediate in all its properties between palmitic and stearic acids.

The so-called margaric acid, obtained by the saponification of natural fats, and regarded by Chevreul* and many other chemists, as a distinct acid having the composition $C_{17}H_{34}O_2$, has been shown by Heintz† to be a mixture, resolvable into stearic acid and other fatty acids of lower melting point, chiefly palmitic acid. Such mixtures of solid fatty acids, or of the corresponding glycerides, cannot be completely resolved into their constituent fats by crystallisation from alcohol, ether, or other solvents, which was the method of separation resorted to in the earlier investigations. The only effectual method of separation is to subject the alcoholic solution of the acids to a series of fractional precipitations with acetate of lead, barium, or magnesium, the stearate then separating out first.

Stearic Acid, $C_{18}H_{36}O_2$, was discovered by Chevreul as a constituent of the more solid fats of the animal kingdom. It is most abundant in these, especially in beef and mutton-suet; but exists also, together with palmitic, myristic acid, &c., in the softer fats, such as the butter of cow's milk, human fat, that of the goose, of serpents, of cantharides, and in spermaceti. It occurs also in vegetable fats, especially those of cacao-beans, of the berries of *Cocculus indicus*, and in shea-butter, obtained from the nuts of *Bassia Parkii*, a tree growing in West Africa. In all these fats it occurs as a glyceride, but in that of cocculus grains also in the free state.

Stearic acid is prepared from beef or mutton-suet, or better from cacao-fat, by saponifying the fat with soda-ley, heating the soap-paste with water and dilute sulphuric acid, removing the separated fatty acids after cooling, washing them with water, and then dissolving them in as small a quantity as possible of hot alcohol. On cooling, the greater part of the solid acid separates out, while the oleic acid remains in solution, and may be separated by subjecting the mass, after draining, to strong pressure, redissolving the residue in a small quantity of alcohol, leaving it to separate by cooling, and again pressing the solid mass. From the mixture of solid fatty acids thus obtained, the stearic acid may be separated in a comparatively pure state, by repeated crystallisation from considerable quantities of alcohol, only the portion which first separates being each time collected. But to obtain pure stearic acid, it is better to dissolve the impure stearic acid (4 parts), melting at 60°, in such a quantity of hot alcohol that nothing will separate out on cooling, even to 0°, and mix the hot liquid with a boiling alcoholic solution of magnesium acetate (1 part). The magnesium-salt which separates on cooling, is pressed and boiled for some time with a large quantity of dilute hydrochloric acid, and the stearic acid thereby separated is repeatedly crystallised from alcohol, till it melts constantly at 69° to 70°.

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* *Recherches sur les corps gras d'origine animale.* Paris, 1823.

† For references to Heintz's memoirs, see Gmelin's Handbook, vol. xv. p. 343.

Stearic acid is also easily prepared from the fat of cocculus-berries, which consists mainly of stearin, by saponifying it with potash, &c. According to Buff and Oudemanns, the best material for the preparation of stearic acid is shea-butter, which contains about 30 per cent. oleic acid, and 70 per cent. stearic, but no other solid fatty acid.

On the large scale, impure stearic acid is prepared for the manufacture of stearin-candles, by saponifying some of the harder fats, generally with lime. The resulting lime-soap, decomposed by sulphuric acid, yields a mixture of fatty acids, which are pressed, first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids. Another method, applied chiefly to palm-oil, consists in decomposing the fat with super-heated steam, as described under GLYCERIN (p. 179). A third method consists in treating the fat with sulphuric acid, and distilling the product.

Pure stearic acid crystallises from alcohol in nacreous laminæ or needles; it is tasteless and inodorous, and has a distinct acid reaction. At low temperatures it is heavier than water, having a specific gravity of 1·01 at 0°; but between 9° and 10° its specific gravity is the same as that of water. It melts at 69°–69·2° to a colourless oil, which on cooling solidifies to a white, fine, scaly, crystalline mass, lamino-crystalline on the fractured surface. When heated, it distils, for the most part, without alteration. *Chlorine* converts it into chlorostearic acid, $C_{18}H_{35}ClO_2$. Heated with *bromine* and water in a sealed tube, it is converted into bromostearic acid, $C_{18}H_{35}BrO_2$, and dibromostearic acid, $C_{18}H_{34}Br_2O_2$.

Stearates.—Stearic acid dissolves in a cold aqueous solution of alkaline carbonate, probably from formation of acid carbonate, and does not expel the carbonic acid and form a mono-acid salt, till heated to about 100°. On the other hand, the stearates are decomposed by most other acids, the separated stearic acid rising to the surface as an oil when the liquid is warm. The stearates have the consistence of hard soaps and plasters, and are mostly insoluble in water. The *normal potassium-salt*, $C_{18}H_{35}O_2K$, separates on cooling from a solution of 1 part stearic acid and 1 part potassium hydrate in 10 parts of water, in white opaque granules. The *acid salt*, $C_{18}H_{35}O_2K.C_{18}H_{36}O_2$, is obtained by decomposing the normal salt with 1000 parts or more of water, and separates in silvery scales from solution in boiling alcohol. *Normal sodium stearate*, $C_{18}H_{35}O_2Na$, is very much like the potassium-salt, but harder. The *acid salt*, $C_{18}H_{35}O_2Na.C_{18}H_{36}O_2$, obtained by decomposing the normal salt with 2000 parts or more of water, separates from the hot solution in nacreous laminæ. The stearates of the earth-metals and heavy metals are insoluble in water, and are obtained by precipitation.

Soaps consist of mixtures of the sodium or potassium salts of stearic, palmitic, oleic, and other fatty or oily acids, and are produced by saponifying tallow, olive oil, and other fats with caustic alkalis. The soda-soaps are called hard soaps: they separate from the alkaline liquor, on addition of common salt, in hard, unctuous masses, which are the soaps in common use: this mode of separation is called *salting out*. The potash-soaps, on the other hand, cannot be thus separated; for, on adding salt to their solution, they are decomposed and converted into soda-soaps; but they are obtained in a semi-solid state by evaporating the solution. The products, called soft soaps, always contain a considerable excess of alkali, and are used for cleansing and scouring when a powerful detergent is required.

Stearic ethers are formed by heating stearic acid with alcohols, monatomic or polyatomic. *Ethyl stearate* $C_2H_5.C_{18}H_{35}O_2$, is most easily obtained by passing hydrochloric acid gas into an alcoholic solution of stearic acid. It resembles white wax, is inodorous and tasteless, melts at 30°, and cannot be distilled without decomposition. It is readily decomposed by boiling with caustic alkalis. There are three glyceryl stearates or stearins, analogous in composition to the palmitins: *Monostearin*, $C_3H_5\left\{\begin{matrix}(OH)_2\\ C_{18}H_{35}O_2\end{matrix}\right.$, prepared by heating a mixture of equal parts of stearic acid and glycerin to 200° in a sealed tube for 36 hours, forms very small white needles, melting at 61°, and solidifying again at 60°.—*Distearin*, $C_3H_5\left\{\begin{matrix}OH\\ (C_{18}H_{35}O_2)_2\end{matrix}\right.$, obtained by heating monostearin with 3 parts of stearic acid to 260° for three hours, forms white microscopic laminæ, melts at 58°, and solidifies at 55°.—*Tristearin*, $C_3H_5(C_{18}H_{35}O_2)_3$, is prepared by heating monostearin with 15 to 20 times its weight of stearic acid to 270° for three hours in a sealed tube; also from various solid natural fats by solution in ether, and repeated crystallisation from the hot solution. It crystallises in masses of white pearly laminæ or needles, inodorous, tasteless, neutral, and volatilising without decomposition under reduced pressure. Both natural and artificial tristearin exhibit three isomeric or allotropic modifications. Stearin separated from ether, melts at 69·7°; but if heated to 73·7° or higher and then cooled, it does not solidify till cooled to 51·7°. It then melts at 52°, and if heated a few degrees higher, passes into a third modification, which does not melt below 64·2°.

Arachidic Acid, $C_{20}H_{40}O_2$, is a fatty acid obtained by saponification of oil of earth-nut (*Arachis hypogæa*). It crystallises in very small, shining scales, melts at 75°, and solidifies again at 73·5° to a radiated crystalline mass. It is but slightly soluble in cold alcohol of ordinary strength, but dissolves easily in boiling absolute alcohol and in ether.

The *silver-salt*, $C_{20}H_{39}O_2Ag$, is a white precipitate, which separates from boiling alcohol in slightly lustrous prisms, not altered by exposure to light. *Ethyl arachidate*, $C_{20}H_{39}O_2.C_2H_5$, is a crystalline mass, melting at 52·5°. Berthelot has obtained three *glyceryl arachidates* or *arachins*, analogous to the stearins, by heating the acid with glycerin in sealed tubes.

Benic or **Behenic Acid**, $C_{22}H_{44}O_2$, is obtained, together with other acids, by saponification of oil of ben, the oil expressed from the fruits of *Moringa Nux Behen*. It is a white crystalline fat, melting at 76°, and solidifying at 70°.

Cerotic Acid, $C_{27}H_{54}O_2$, is the essential constituent of *cerin*, the portion of bees'-wax which is soluble in boiling alcohol. It is prepared by heating the wax several times in succession with boiling alcohol, till the deposit which forms on cooling melts at 70° or 72°, and may be further purified by precipitating it from the boiling alcoholic solution with lead acetate, decomposing the precipitate with strong acetic acid, and crystallising the separated acid from boiling alcohol. Cerotic acid is also produced by the dry distillation of Chinese wax, which consists of ceryl cerotate, $C_{27}H_{53}O.{}_2C_{27}H_{55}$, or by melting that substance with potash, and decomposing the resulting potassium-salt with an acid (p. 160).

Pure cerotic acid crystallises in small grains, melting at 78°, and distilling without alteration. Chlorine converts it into chlorocerotic acid, $C_{27}H_{42}Cl_{12}O_2$, a thick transparent gum of a pale yellow colour.

Ceryl cerotate, or *Chinese wax*, is produced on certain trees in China by the puncture of a species of *coccus*. It is crystalline, of a dazzling whiteness, like spermaceti, melts at 82°; dissolves in alcohol; yields cerotic acid and cerylene, $C_{27}H_{54}$, by dry distillation. It is used in China for making candles.

Melissic Acid, $C_{30}H_{60}O_2$, the highest known member of the fatty series, is obtained by heating myricyl alcohol (p. 161) with potash-lime:

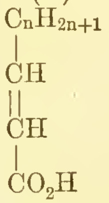
$$C_{30}H_{62}O_2 + KOH = C_{30}H_{59}O_2K + 2H_2.$$

It bears considerable resemblance to cerotic acid, but melts at a higher temperature, viz., at 88° or 89°. The *silver-salt*, $C_{30}H_{59}O_2Ag$, is a white precipitate.

Monatomic Acids, $C_nH_{2n-2}O_2$.—Acrylic Series.

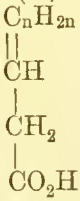
This series comprises three isomeric groups of acids, which may be represented by the following general formulæ, in which *n* and *p* denote any whole numbers from 0 upwards:*

(1.)



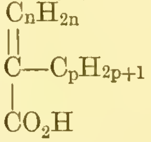
$$\begin{array}{l} C_nH_{2n+1} \\ | \\ CH \\ \| \\ CH \\ | \\ CO_2H \end{array}$$

(2.)



$$\begin{array}{l} C_nH_{2n} \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

(3.)



$$\begin{array}{l} C_nH_{2n} \\ \| \\ C—C_pH_{2p+1} \\ | \\ CO_2H \end{array}$$

Of the acids of the first group, called normal acrylic acids, some occur, mostly as glycerides, in vegetable and animal organisms, others are formed artificially by special processes. Most of them are oily liquids. The known acids of this group are :

Acrylic acid, .	. $C_3H_4O_2$	Physetoleic acid,	. $C_{16}H_{30}O_2$
Crotonic acid, .	. $C_4H_6O_2$	Hypogæic acid,	
Angelic acid, .	. $C_5H_8O_2$	Gaïdic acid,	
Pyroterebic acid,	. $C_6H_{10}O_2$	Oleic acid,	. $C_{18}H_{34}O_2$
? Damaluric acid,	. $C_7H_{12}O_2$	Elaïdic acid,	
? Damolic acid, .	. $C_{13}H_{24}O_2$	Doeglic acid, .	. $C_{19}H_{36}O_2$
Moringic acid,	. $C_{15}H_{28}O_2$	Brassic acid,	. $C_{22}H_{42}O_2$
Cimicic acid,		Erucic acid,	

Of the acids of the second group only one is at present known, viz., isocrotonic acid, $C_4H_6O_2 = CH_2 = CH—CH_2—CO_2H$ [n=1].

The acrylic acids of the third group are formed by a general synthetical process, viz., by abstraction of the elements of water from certain acid ethers or alcoholic acids, having the composition of oxalic

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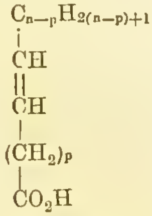
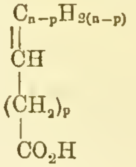
* The most general formulæ by which the structure of these acids can be represented are the following :—

(1, *a*)



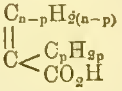
$$\begin{array}{l} C_{n-p}H_{2(n-p)+1} \\ | \\ CH \\ \| \\ CH \\ | \\ (CH_2)_p \\ | \\ CO_2H \end{array}$$

(2, *a*)



$$\begin{array}{l} C_{n-p}H_{2(n-p)} \\ \| \\ CH \\ | \\ (CH_2)_p \\ | \\ CO_2H \end{array}$$

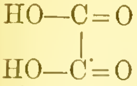
(3, *a*)



$$\begin{array}{l} C_{n-p}H_{2(n-p)} \\ \| \\ C{<}\begin{array}{l} C_pH_{2p} \\ CO_2H \end{array} \end{array}$$

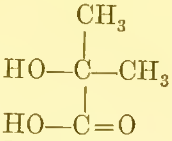
The first of these formulæ is reducible to $C_{n+3}H_{2n+4}O_2$ or $C_{n+3}H_{2(n+3)-2}O_2$, and the second and third to $C_{n+2}H_{2n+2}O_2$ or $C_{n+2}H_{2(n+2)-2}O_2$, both of which are included under the general formula of the series $C_mH_{2m-2}O_2$. In all the known acids of the first group, however, except perhaps angelic acid (p. 308), the value of p = 0, and in the only known acid of the second group, viz., isocrotonic acid, p=1, so that for these known acids the two formulæ are reduced to the simpler forms given in the text.

acid, $C_2H_2O_4$, in which 1 atom of oxygen is replaced by 2 atoms of a monatomic alcohol-radicle, C_nH_{2n+1}; thus:



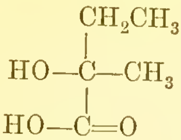
$$\begin{array}{l}HO—C=O\\ \quad\ \ |\\ HO—C=O\end{array}$$

Oxalic acid.



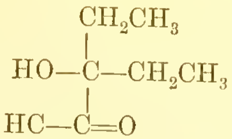
$$\begin{array}{l}\qquad\ \ CH_3\\ \qquad\ \ |\\ HO—C—CH_3\\ \qquad\ \ |\\ HO—C=O\end{array}$$

Dimethoxalic acid.



$$\begin{array}{l}\qquad\ \ CH_2CH_3\\ \qquad\ \ |\\ HO—C—CH_3\\ \qquad\ \ |\\ HO—C=O\end{array}$$

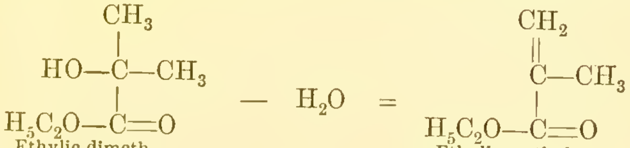
Ethomethoxalic acid.



$$\begin{array}{l}\qquad\ \ CH_2CH_3\\ \qquad\ \ |\\ HO—C—CH_2CH_3\\ \qquad\ \ |\\ HC—C=O\end{array}$$

Diethoxalic acid.

Now, when the ethylic ethers of these acids are treated with phosphoric oxide or phosphorus trichloride, they give up a molecule of water (H_2O), at the expense of one of the molecules of hydroxyl (OH) and of an atom of hydrogen abstracted from one of the monad alcohol-radicles, which is thereby converted into a dyad radicle (an olefine) capable of saturating the unit of equivalence of the carbon-atom set free by abstraction of the hydroxyl. The product is the ethylic ether of an acrylic acid of the third group; thus:



$$\underset{\text{Ethylic dimethoxalate.}}{\begin{array}{l}\qquad\quad\ CH_3\\ \qquad\quad\ |\\ \quad HO—C—CH_3\\ \qquad\quad\ |\\ H_5C_2O—C=O\end{array}} \quad - \quad H_2O \quad = \quad \underset{\text{Ethylic methylacrylate.}}{\begin{array}{l}\qquad\quad\ CH_2\\ \qquad\quad\ \|\\ \qquad\quad\ C—CH_3\\ \qquad\quad\ |\\ H_5C_2O—C=O\end{array}}$$

The ethylic ether thus formed is converted into methacrylic acid by saponification with potash in the usual way. In this manner the following acids have been obtained:

Methacrylic acid, $CH_2=C<\begin{matrix}CH_3\\COOH\end{matrix}$, isomeric with Crotonic acid.

Methylcrotonic acid, $C_2H_4=C<\begin{matrix}CH_3\\COOH\end{matrix}$, isomeric with Angelic acid.

Ethylcrotonic acid, $C_2H_4=C<\begin{matrix}CH_2CH_3\\COOH\end{matrix}$, isomeric with $\left\{\text{Pyroterebic acid.}\right.$

There might of course be an ethacrylic acid isomeric with methyl-crotonic acid, and a propyl-acrylic acid isomerie with ethyl-crotonic acid, but these have not yet been obtained.

The individual acids of the three groups differ from one another according to the values of *n* and *p*, and those which contain the radicle C_3H_7 and its higher homologues, are susceptible of further modifications according to the structure of these radicles.

The acids of all three series, when fused with potash, are resolved, with evolution of hydrogen, into two acids of the fatty series:

$$\underset{\text{Angelic.}}{C_5H_8O_2} + 2H_2O = \underset{\text{Propionic.}}{C_3H_6O_2} + \underset{\text{Acetic.}}{C_2H_4O_2} + H_2$$

$$\underset{\text{Oleic.}}{C_{18}H_{34}O_2} + 2H_2O = \underset{\text{Palmitic.}}{C_{16}H_{32}O_2} + \underset{\text{Acetic.}}{C_2H_4O_2} + H_2$$

generally:

$$C_nH_{2n-2}O_2 + 2H_2O = C_{n-p}H_{2(n-p)}O_2 + C_pH_{2p}O_2 + H_2.$$

The manner in which this splitting up of the molecule takes place differs, however, according to the group to which the acid belongs. In the decomposition of an acrylic acid of the first group, one of the products formed is always acetic acid; in the second, one of the products is always propionic acid; while in the third the two products may be any members of the fatty series of acids.

The final result of the action above mentioned is in fact to add 2 atoms of hydrogen and 2 atoms of oxygen to the molecule $C_nH_{2n-2}O_2$. Now, if in an acid of the first group, represented by the formula, $C_nH_{2n+1}—CH\overset{\vdots}{\underset{\vdots}{=}}CH—CO_2H$, we suppose H_2 to be added to the right of the dotted line, we get $CH_3—CO_2H$, which is the formula of acetic acid, while the addition of O_2 to the left of the dotted line gives $C_nH_{2n+1}—CO_2H$, which is also the formula of a fatty acid. Similarly the addition of H_2 on the right of the formula of the second group, $C_nH_{2n}\overset{\vdots}{\underset{\vdots}{=}}CH—CH_2—CO_2H$, gives $CH_3—CH_2—CO_2H$, which is the formula of propionic acid, while the addition of O_2 on the left gives $C_nH_{2n}O_2$, which represents another fatty acid.

The acrylic acids are also converted into fatty acids by the action of nascent hydrogen, *e.g.*, crotonic acid, $C_4H_6O_2$, into butyric acid, $C_4H_8O_2$.

Acrylic Acid, $C_3H_4O_2 = CH_2=CH—CO_2H$ [n = 0 in formula 1].—This acid is the lowest possible member of the series, and does not admit of isomeric modifications. It is produced—(1) By oxidising its aldehyde (acrolein), C_3H_4O, with moist silver oxide; (2) From α or β iodopropionic acid, $CH_3.CHI.CO_2H$, or $CH_2I.CH_2.CO_2H$, by heating alone, or with alcoholic potash, whereby HI is abstracted; (3) By the action of nascent hydrogen (zinc and sulphuric acid) on β-dibromopropionic acid:

$$CH_2Br—CHBr—CO_2H + H_2 = 2HBr + CH_2=CH—CO_2H.$$

Acrylic acid is a colourless liquid, having a pungent, slightly aromatic odour, and miscible in all proportions with water. It solidifies at low temperatures, melts at 7°, and boils at 139°–140°. Nascent hydrogen converts it into propionic acid. It unites with bromine, forming β-dibromopropionic acid, and with the haloïd acids to form the β-substitution-products of propionic acid. By fusion with potash it is resolved into formic and acetic acids.

The metallic acrylates, excepting the silver salt, are very soluble in water: they decompose at 100°. The *silver salt*, $C_3H_3O_2Ag$, and the *lead salt*, $(C_3H_3O_2)_2Pb$, crystallise in shining needles.

Ethyl Acrylate, $CH_2=CH—CO_2C_2H_5$, prepared from the ethylic ether of β-dibromopropionic acid by the action of zinc and sulphuric acid, is a pungent-smelling liquid, having a specific gravity of 0·925 at 0°, and boiling at 102°.

Chloracrylic Acid, $C_3H_3ClO_2$, prepared by treating dichloropropionic acid with baryta-water, crystallises in slender needles, which melt at 65°.—*Bromacrylic Acid*, $C_3H_3BrO_2$. Of this acid there are two modifications, $CH_2{=}CBr{-}CO_2H$ and $CHBr{=}CH{-}CO_2H$, obtained respectively from α- and β-dibromopropionic acid. The former melts at 70°, and unites with hydrobromic acid, reproducing α-dibromopropionic acid.

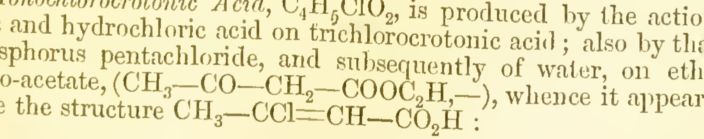
Crotonic Acids, $C_4H_6O_2 = C_3H_5{-}CO_2H$.—Of these acids there are three modifications, viz.:

(1.) **Solid Crotonic Acid**, $CH_3{-}CH{=}CH{-}CO_2H$.—This acid is formed—α. By oxidation of its aldehyde, $CH_3{-}CH{=}CH{-}COH$ (p. 255); β. By the dry distillation of β-oxybutyric acid, $CH_3{-}CH(OH){-}CH_2{-}CO_2H$ (abstraction of OHH); γ. By the action of alcoholic potash on α-bromobutyric acid, $CH_3{-}CH_2{-}CHBr{-}CO_2H$; δ. From allyl iodide by conversion into the cyanide, and distillation of the latter with potash. Now allyl iodide has the structure $CH_2{=}CH{=}CH_2I$ (p. 163), and therefore the cyanide might be expected to be $CH_2{-}CH{-}CH_2CN$, and the acid obtained from it, $CH_2{=}CH{-}CO_2OH$, which is the structure of isocrotonic acid. But as the acid obtained in this manner is identical in its properties with that which is produced by the first three reactions, it must be inferred that, either in the conversion of the allyl iodide into cyanide, or of the latter into the acid, a transposition of atoms has taken place within the molecule.

Solid crotonic acid crystallises in slender woolly needles, or in large plates, melts at 72°, boils at 182°, and dissolves in 12 parts of water at 20°. Nascent hydrogen converts it into normal butyric acid. It unites with hydrogen bromide, forming monobromobutyric acid, and with bromine to form dibromobutyric acid. By oxidation with nitric acid, it is resolved into acetic and oxalic acids, and by fusion with potash, into two molecules of acetic acid:

$$CH_3{-}CH{=}CH{-}CO_2H + 2H_2O = 2(CH_3CO_2H) + H_2.$$

Monochlorocrotonic Acid, $C_4H_5ClO_2$, is produced by the action of zinc and hydrochloric acid on trichlorocrotonic acid; also by that of phosphorus pentachloride, and subsequently of water, on ethylic aceto-acetate, $(CH_3{-}CO{-}CH_2{-}COOC_2H_5{-})$, whence it appears to have the structure $CH_3{-}CCl{=}CH{-}CO_2H$:



$$\begin{array}{l}CH_3\\CO\\CH_2\\COOC_2H_5\end{array} + 2PCl_3Cl_2 = 2PCl_3O + C_2H_5Cl + HCl + \begin{array}{l}CH_3\\CCl\\\|\\CH\\COCl\end{array}$$

and

$$CH_3.CCl{=}CH.COCl + HOH = HCl + CH_3.CCl{=}CH{-}COOH.$$

This acid dissolves in 35 parts of water at 19°, melts at 94°, and boils at 206°–210°. Sodium amalgam converts it into crotonic acid.

Trichlorocrotonic Acid, $C_4H_3Cl_3O_2$, produced by oxidation of the corresponding aldehyde with cold strong nitric acid, melts at 44°.

(2.) **Isocrotonic Acid,** $CH_2{=}CH{-}CH_2{-}CO_2H$ (Geuther's *quartenylic acid*), formed from its chloro-derivative (*infra*) by the action of sodium amalgam, is a non-solidifying liquid, having a specific gravity of 1·018 at 25°, and boiling at 172°. When heated in a sealed tube to 170°–180°, it is converted into solid crotonic acid. When fused with potash, it is resolved, not as might be expected, into propionic and formic acids, but, in consequence of the transformation by heat just mentioned, into two molecules of acetic acid.

Chlorisocrotonic acid, $CH_2{=}CCl{-}CH_2{-}CO_2H$, is produced, together with chlorocrotonic acid, by the action of phosphorus pentachloride and water on ethylic aceto-acetate. It forms crystals slightly soluble in water, sublimes at ordinary temperatures, melts at 59·5°, and boils at 195°.

(3.) **Methacrylic Acid,** $CH_2{=}C{<}\begin{matrix}CH_3\\CO_2H\end{matrix}$ [n = 1, p = 1 in formula 3, p. 304], is formed by the action of phosphoric oxide or phosphorus trichloride on ethylic dimethoxalate (p. 305), and by that of phosphorus trichloride on oxyisobutyric acids:

$$\begin{matrix}H_3C\\H_3C\end{matrix}{>}C{<}\begin{matrix}OH\\CO_2H\end{matrix} = H_2O + \begin{matrix}H_2C\\H_3C\end{matrix}{>}C{-}CO_2H.$$

It is a liquid which does not solidify at 0°. By fusion with potash it is resolved into formic and propionic acids.

Five-carbon Acrylic Acids, $C_5H_8O_2 = C_4H_7.CO_2H$.—Of these acids, two only are known, namely, angelic and methylcrotonic acid.

Angelic Acid exists in the root of the archangel (*Angelica Archangelica*), and in sumbul or moschus root, a drug imported from Asia Minor, and probably also belonging to an umbelliferous plant. It is obtained from archangel root, by boiling the root with lime and water, and distilling the strained and concentrated liquid with dilute sulphuric acid. It is also produced by heating the essential oil of chamomile, which consists of angelic aldehyde together with a hydrocarbon, with potassium hydroxide:

$$C_5H_8O + KOH = C_5H_7KO_2 + H_2.$$

Also, together with oreoselin, by treating peucedanin or imperatorin (a neutral substance contained in the root of *Imperatoria Ostruthium*, and some other umbelliferous plants), with alcoholic potash:

$$\underset{\text{Peucedanin.}}{C_{12}H_{12}O_3} + KOH = \underset{\substack{\text{Potassium}\\\text{angelate.}}}{C_5H_7KO_2} + \underset{\text{Oreoselin.}}{C_7H_6O_2}$$

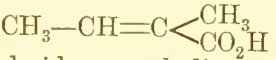
Angelic acid crystallises in long prisms and needles, melts at 45°, boils at 190°, and distils without decomposition. It has an aromatic taste and odour, dissolves sparingly in cold, abundantly in hot water, also in alcohol and ether.

It unites with *bromine*, forming a dibromovaleric acid, $C_5H_8Br_2O_2$, which is reconverted by sodium-amalgam into angelic acid. It is not altered by nascent hydrogen, but when heated with concentrated *hydriodic acid* and a little phosphorus, it is converted into normal valeric acid. By fusion with *potash* it is resolved into acetic and propionic acids, a mode of decomposition which is consistent with either of the two following structural formulæ of the acid:

$$C_2H_5—CH{=}CH—CO_2H\ ^{*}, \text{ or } CH_3—CH{=}CH—CH_2—CO_2H\ .^{\dagger}$$

The angelates of the alkali-metals are soluble in water and in alcohol. *Calcium angelate*, $Ca(C_5H_7O_2)_2+aq.$, forms shining, very soluble laminæ. The *lead-salt*, $Pb(C_5H_7O_2)_2$, is a white precipitate.

Potassium angelate treated with phosphorus oxychloride yields angelic oxide, or anhydride, $(C_5H_7O)_2O$, which is a viscid uncrystallisable oil, boiling at 240°.

Methyl-crotonic Acid,  $CH_3—CH{=}C{<}^{CH_3}_{CO_2H}$, formed by the action of phosphorus trichloride on ethylic methyl-ethyloxalate (p. 305), is very much like angelic acid, but melts at 62°. By fusion with potash it is resolved into acetic and propionic acids.

Identical with this is the so-called tiglic acid, which is contained as a glyceride, together with those of butyric, valeric, and other fatty acids, in the oil of *Croton Tiglium.*

Six-carbon Acids, $C_6H_{10}O_2=C_5H_9.CO_2H$.—1. *Pyroterebic acid* is formed by dry distillation of terebic acid, $C_7H_{10}O_4$ (one of the products of the action of nitric acid on turpentine-oil). It is an oily liquid, smelling like butyric acid, having a specific gravity of 1·01, and boiling at 210°. By fusion with potash it is resolved into acetic and isobutyric acids.

2. *Hydrosorbic acid* is formed by the action of sodium-amalgam on sorbic acid, $C_6H_8O_2$. It is a liquid having a sudorific odour, a specific gravity of 0·969 at 19°, and boiling at 204·5°. By fusion with potash it is resolved into acetic and normal butyric acids. This and the preceding acid are therefore represented by the following formulæ:

$$CH_3—CH_2—CH_2—CH{=}CH—CO_2H$$

Hydrosorbic.

$$CH(CH_3)_2—CH{=}CH—CO_2H$$

Pyroterebic.

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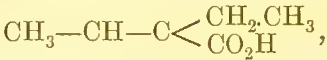
[*] $n=2$, $p=0$, in formula 1, *a* (p. 304, footnote).

[†] $n=2$, $p=1$, in the same.



3. *Ethyl-crotonic acid,* $CH_3—CH—C<\genfrac{}{}{0pt}{}{CH_2.CH_3}{CO_2H}$, is formed from the ethylic ether of diethoxalic acid (p. 305), by the action of phosphorus trichloride, or by heating with hydrochloric acid to 130°–150°. It crystallises in shining square prisms, has an aromatic odour, sublimes even at ordinary temperatures, and melts at 41·5°. By fusion with potash it is resolved into acetic and normal butyric acids. Its salts decompose, even during the evaporation of their aqueous solutions.

Seven- to Fifteen-Carbon Acids.—Damaluric acid, $C_7H_{12}O_2$, and Damolic acid, $C_{13}H_{24}O_2$, are volatile acids, said to exist in the urine of cows and horses.—Moringic acid, $C_{15}H_{28}O_2$, is an oily acid obtained, together with palmitic, stearic, and benic acids, by the saponification of oil of ben (p. 303).—Cimicic acid, $C_{15}H_{28}O_2$, is a yellow crystallisable acid, having a rancid odour, extracted by alcohol and ether from a kind of bug (*Rhaphigaster punctipennis*).

Hypogæic Acid, $C_{16}H_{30}O_2$, is contained as a glyceride, together with palmitin and arachin, in oil of earth-nut (*Arachis hypogæa*). To obtain it, the mixture of fatty acids obtained by saponifying the oil is dissolved in alcohol; the palmitic and arachidic acids are precipitated by ammonia and magnesium acetate; the filtrate is mixed with ammonia and lead acetate; the lead precipitate is decomposed by hydrochloric acid; and the separated hypogæic acid is dissolved out by ether. It is also produced by oxidation of axinic acid, ($C_{18}H_{28}O_2$), an acid obtained by saponification of *age* or *axin*, a fatty substance contained in the Mexican plant *Coccus Axin.*—Hypogæic acid crystallises from ether in stellate groups of needles, melting at 34° or 35°, easily soluble in alcohol and ether. Its *potassium* and *sodium salts* are soluble in water; the *barium salt* is soluble in hot, insoluble in cold water; the *copper* and *silver salts* are obtained by precipitation. The *ethylic ether,* $C_{16}H_{29}O_2.C_2H_5$, is a yellow oil, not volatile without decomposition.

Nitrous acid converts hypogæic acid into the isomeric or allotropic compound, Gaïdic acid, related to it in the same manner as elaïdic acid to oleic acid. It forms a colourless crystalline mass which melts at 38°.

Physetoleic acid, a crystalline acid obtained from sperm-oil, is isomeric, if not identical, with hypogæic acid; it melts at 30°, and solidifies at 28°.

Oleic Acid, $C_{18}H_{34}O_2$.—This acid, the most important of the series, is obtained by saponification of olein, the fluid constituent of most natural fats and fixed oils.

To obtain pure oleic acid, olive or almond oil is saponified with potash; the soap is decomposed by tartaric acid; and the separated fatty acid, after being washed, is heated for some hours in the water-bath, with half its weight of lead oxide previously reduced to fine powder. The mixture is then well shaken up with about twice its bulk of ether, which dissolves the oleate of lead, and leaves the stearate; the liquid after standing for some time, is decanted and mixed with hydrochloric acid; the oleic acid thereby eliminated dissolves in the ether; and the ethereal solution which rises to the surface of the water is decanted, mixed with water, and freed from ether by distillation.

Large quantities of crude oleic acid are now obtained in the manufacture of stearine candles, by treating with dilute sulphuric acid the lime-soap resulting from the action of lime upon tallow. The fatty acids resulting from the decomposition are washed with hot water, and solidify in a mass on cooling; and this mass, when subjected to pressure, yields a liquid rich in oleic acid, but still retaining a considerable quantity of stearic acid. After remaining for some time in a cold place, it deposits a quantity of solid matter, and the liquid decanted from this is sent into the market as *oleic acid* or *red oil.* It may be purified by the process just described.

Oleic acid crystallises from alcoholic solution in dazzling white needles, melting at 14° to a colourless oil, which solidifies at 4° to a hard, white, crystalline mass, expanding considerably at the same time. Specific gravity = 0·898 at 19°. The acid volatilises in a vacuum without decomposition. It is tasteless and inodorous, and reacts neutral when unaltered (not oxidised), also in alcoholic solution. It is insoluble in water, very soluble in alcohol, and dissolves in all proportions in ether. Cold strong sulphuric acid dissolves it without decomposition. It dissolves solid fats, stearic acid, palmitic acid, &c., and is dissolved by bile, with formation of a soap and strong acid reaction.

Oleic acid, in the solid state, oxidises but slowly in the air; but when melted, it rapidly absorbs oxygen, acquiring a rancid taste and smell and a decided acid reaction. Its decomposition by fusion with potash has been already mentioned. *Chlorine* and *bromine*, in presence of water, convert it into dichloroleic and dibromoleic acids. Bromine, added by drops to fused oleic acid, forms tribromoleic acid, $C_{18}H_{31}Br_3O_2$.

Strong *nitric acid* attacks oleic acid with violence, giving off red nitrous vapours, and producing volatile acids of the series $C_nH_{2n}O_2$, viz., acetic, propionic, butyric, valeric, caproic, œnanthylic, caprylic, pelargonic, and rutic acids; also fixed acids of the series $C_nH_{2n-2}O_4$, viz., suberic, pimelic, adipic, lipic, and azelaic acids, the number and proportion of these products varying with the duration of the action.

Nitrous acid converts oleic acid into a solid isomeric or allotropic modification, called elaïdic acid.

Oleates.—The formula of the neutral oleates is $M'C_{18}H_{33}O_2$, or $M''(C_{18}H_{33}O_2)_2$, according to the quantivalence of the metal: there are likewise acid oleates. The neutral oleates of the alkali-metals are soluble in water, and not so completely precipitated from their solutions by the addition of another soluble salt, as the stearates and palmitates. The acid oleates are liquid and insoluble in water. The oleates dissolve in cold absolute alcohol and in ether, a property by which they may be distinguished and separated from the stearates and palmitates.

Oleins.—Oleic acid forms three glycerides, viz., monolein, $(C_3H_5)(OH)_2(C_{18}H_{33}O_2)$; diolein, $(C_3H_5)(OH)(C_{18}H_{33}O_2)_2$; and triolein, $(C_3H_5)(C_{18}H_{33}O_2)_3$, which are produced by heating oleic acid and glycerin together in sealed tubes, in various proportions. The first two solidify at about 15°.

The olein of animal fats, of olive oil, and of several other oils, both animal and vegetable, which do not dry up in the air by slow oxidation, but are converted into viscid masses having a rancid odour and acid reaction (non-drying oils), appears to be identical with triolein, but there is great difficulty in obtaining it pure. Olive oil, cooled to 4° or a lower temperature, deposits a large quantity of solid fat, consisting mainly of palmitin (originally called *margarin*, from its pearly lustre), and the oil filtered therefrom consists mainly of olein. A purer olein is obtained by treating olive oil with a cold strong solution of caustic soda, which saponifies the solid fats, and leaves the olein unaltered. Olein, subjected to dry distillation, yields gaseous products, liquid hydrocarbons, acrolein, and sebic acid.

Appendix to Oleic Acid.—Some non-drying oils contain the glycerides of acids homologous with oleic acid; such is the case, as already observed, with croton oil, earth-nut oil, and sperm oil. Doegling train-oil, obtained from the doegling or bottle-nosed whale *(Balæna rostrata)*, yields doeglic acid, $C_{19}H_{36}O_2$. Colza-oil, obtained from the seeds of certain species of *Brassica*, especially the summer rape or colza, *Brassica campestris*, var. *oleifera*, yields brassic acid, $C_{22}H_{42}O_2$; and the oil of black mustard-seed yields a similar and probably identical acid, called erucic acid.

Drying oils, such as linseed, poppy, hemp, and nut oils, contain the glycerides of linoleic acid, $C_{16}H_{28}O_2$, which may be prepared by saponifying linseed oil with potash, precipitating the aqueous solution of the resulting potassium salt with calcium chloride, dissolving out the calcium linoleate with ether, and decomposing it with hydrochloric acid. Linoleic acid is a yellowish oil of specific gravity, 0·921, not altered by nitrous acid.

Castor oil, which is a non-drying oil, contains the glyceride of ricinoleic acid, $C_{18}H_{34}O_3$, which, when separated, forms a colourless oil, solidifying at 0°, and converted by nitrous acid into a solid modification, ricinelaïdic acid, which melts at 50°. By dry distillation it is resolved into œnanthylic acid and œnanthol, and when heated with excess of caustic potash or soda, it yields secondary octyl alcohol, together with sebic acid and free hydrogen (p. 158)

Monatomic Acids, $C_nH_{2n-4}O_2$.—The known acids of this series are :

Tetrolic acid,	$C_4H_4O_2$	Stearolic acid,	$C_{18}H_{32}O_2$
Sorbic acid,	$C_6H_8O_2$	Behenolic acid,	$C_{22}H_{40}O$.
Palmitolic acid,	$C_{16}H_{28}O_2$		

They are formed from the acids of the preceding series by abstraction of 2 atoms of hydrogen, which is effected by the action of alcoholic potash on the chlorine or bromine compounds or derivatives of those acids; *e.g.*,

$$\underset{\text{Bromocrotonic acid.}}{C_4H_5BrO_2} + KOH = KBr + H_2O + \underset{\text{Tetrolic acid.}}{C_4H_4O_2}.$$

$$\underset{\text{Bromide of crotonic acid.}}{C_4H_6Br_2O_2} + 2KOH = 2KBr + 2H_2O + \underset{\text{Tetrolic acid.}}{C_4H_4O_2}$$

They contain 4 atoms of hydrogen less than the corresponding fatty acids, and are therefore unsaturated compounds of the second order, capable of uniting with 2 or with 4 atoms of a halogen-element.

Tetrolic Acid, $C_4H_4O_2$, produced as above from monochlorocrotonic acid, crystallises in deliquescent rhombic plates, easily soluble in alcohol and ether. It melts at 76·5°, and boils at 203°.

Sorbic Acid, $C_6H_8O_2$, occurs in the unripe berries of the mountain ash (*Sorbus aucuparia*), from which it may be obtained by mixing the juice with milk of lime and distilling. It then passes over as an oily liquid, which solidifies when boiled with strong hydrochloric acid, or when warmed with potash.

Sorbic acid crystallises in long needles, melts at 134·5°, decomposes when distilled alone, but is easily volatilised with vapour of water. It is nearly insoluble in cold water, but dissolves with moderate facility in hot water and in alcohol. *Nascent hydrogen* converts it into hydrosorbic acid, $C_6H_{10}O_2$. With *bromine* it forms the compounds $C_6H_8Br_2O_2$ and $C_6H_8Br_4O_2$, melting respectively at 95° and 183°.

The metallic sorbates are crystallisable. The *ammonium salt* crystallises in long needles; the *barium salt*, $(C_6H_7O_2)_2Ba$, and the *calcium salt*, $(C_6H_7O_2)_2Ca$, form silvery scales. The *silver salt*, $C_6H_7O_2Ag$, is a crystalline precipitate. The *ethylic ether*, $C_6H_7O_2.C_2H_5$, is an aromatic liquid, boiling at 195·5

Palmitolic Acid, $C_{16}H_{28}O_2$, prepared from the dibromide of hypogæic acid, or of its isomeride, gaïdic acid, crystallises in shining needles which melt at 42°. It unites with 2 and 4 atoms of bromine, but is not altered by nascent hydrogen.

Stearolic Acid, prepared in like manner from the dibromide of oleic or elaïdic acid, crystallises in long prisms, which melt at 48°, and distil almost without decomposition. It is insoluble in water, but dissolves readily in alcohol and ether. It unites with 2 and 4 atoms of *bromine*, but is not altered by nascent hydrogen. By carefully regulated fusion with *potash*, it is resolved into acetic and hypogæic acids; at higher temperatures myristic acid is produced.

Behenolic Acid, $C_{22}H_{40}O_2$, from dibromide of erucic or brassic acid (p. 312), forms shining needles, melting at 75°.

The last three acids, heated with fuming nitric acid, are converted into monobasic acids of the form $C_nH_{2n-4}O_4$, viz.:

	Palmitoxylic.	Stearoxylic.	Behenoxylic.
	$C_{16}H_{28}O_4$	$C_{18}H_{32}O_4$	$C_{22}H_{40}O_4$
melting at	67°	86°	90°

These acids crystallise in shining plates or scales.

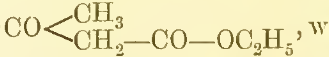
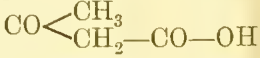
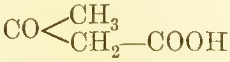
CARBOKETONIC ACIDS.

These acids are derived from ethyl acetate and other compound ethers of the fatty series. When sodium is heated with ethyl acetate, it dissolves, with little or no evolution of hydrogen, and the whole solidifies on cooling to a crystalline mass of sodium ethylate and ethylic acetosodacetate, $C_6H_9NaO_3$. The reaction is either

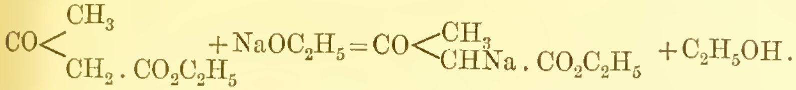
$$2(C_2H_3O.OC_2H_5) + 2Na = C_6H_9NaO_3 + NaOC_2H_5 + H_2$$

$$\text{or} \quad 3(C_2H_3O.OC_2H_5) + 4Na = C_6H_9NaO_3 + 3NaOC_2H_5.$$

The quantity of hydrogen evolved in this reaction varies considerably according to the temperature and pressure under which it takes place, and the proportions of the materials used; sometimes no gas is evolved, showing that the reaction takes place according to the second equation, and under no circumstances yet observed is the quantity of hydrogen given off, exactly equivalent to the sodium dissolved, as it should be if the reaction took place entirely according to the first equation. It is most probable, therefore, that the two reactions generally take place together.

Ethylic acetosodacetate (Wanklyn's *sodium-triacetyl*) crystallises in shining scales. When treated with acetic acid, it is converted into the compound $C_6H_{10}O_3$ or  $CO<\begin{smallmatrix}CH_3\\ CH_2—CO—OC_2H_5\end{smallmatrix}$, which is the ethylic ether of aceto-acetic acid,  $CO<\begin{smallmatrix}CH_3\\ CH_2—CO—OH\end{smallmatrix}$ derived from acetic acid, $CO<\begin{smallmatrix}CH_3\\ OH\end{smallmatrix}$, by substitution of acetyl, $CH_3.CO$, for one of the hydrogen-atoms in the methyl group. This acid is not known in the free state; when separated from its ether by boiling with alkalis or acids, it is resolved into acetone and carbon dioxide,  $CO<\begin{smallmatrix}CH_3\\ CH_2—COOH\end{smallmatrix} = CO(CH_3)_2 + CO_2$.

The ethylic ether, $C_6H_{10}O_3$ (also called ethyl-diacetic acid), is a liquid having an odour of strawberries, a specific gravity of 1·03, and boiling at 180·8°. By the action of sodium or of sodium ethylate, it is converted into ethylic acetosodacetate, the compound already mentioned as a direct product of the action of sodium on acetic ether:

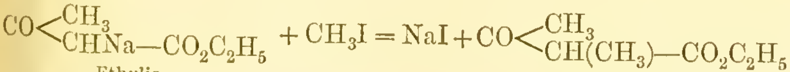


$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2\,.\,CO_2C_2H_5}\end{array} + \mathrm{NaOC_2H_5} = \mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CHNa\,.\,CO_2C_2H_5}\end{array} + \mathrm{C_2H_5OH}.$$

The *potassium salt* is obtained in a similar manner. The *barium salt*, $(C_6H_9O_3)_2Ba$, obtained by dissolving the ether in baryta-water, is easily soluble in water. From its solution the corresponding salts of the heavy metals may be obtained by double decomposition.

Methylic Aceto-acetate, $C_5H_8O_3 = \mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2.CO_2CH_3}\end{array}$, obtained by the action of sodium on methyl acetate, &c., is a colourless, pungent-smelling liquid, which boils at 170°, and has a specific gravity of 1·037 at 9°. It has a faint acid reaction, dissolves sparingly in water, freely in alcohol and ether; produces a dark-red coloration with ferric chloride; is resolved, by boiling with hydrochloric acid or with alkalis, into acetone, carbon dioxide, and methyl alcohol. Its *sodium salt*, $C_5H_7O_3Na$, crystallises in shining needles. The *barium salt*, $(C_5H_7O_3)_2Ba$, is obtained by dissolving the ether in baryta-water. Its aqueous solution mixed with cupric acetate yields the *copper salt* $(C_5H_7O_3)_2Cu + 2H_2O$ in green crystals, slightly soluble in water.

By treating the sodium derivatives of these aceto-acetic ethers with the iodides of alcohol radicles, new ethers are obtained, in which the sodium of the original compound is replaced by an alcohol-radicle, *e.g.*,

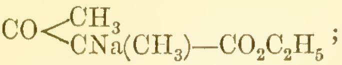


$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CHNa{-}CO_2C_2H_5}\end{array} + \mathrm{CH_3I} = \mathrm{NaI} + \mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH(CH_3){-}CO_2C_2H_5}\end{array}$$

Ethylic acetosodacetate. Ethylic methylacetacetate.

In these last ethers an atom of hydrogen may also be replaced by sodium, by the action of metallic sodium or of sodium ethylate, producing compounds like

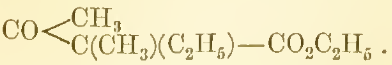
Ethylic Sodio-methylaceto-acetate,



$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CNa(CH_3){-}CO_2C_2H_5}\end{array};$$

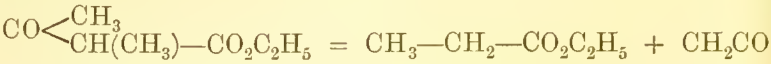
and in these again the sodium may be replaced by alcohol-radicles, yielding, for example,

Ethylic Methylethyl-aceto-acetate,



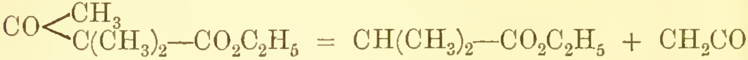
$$\mathrm{CO}<\begin{array}{l}\mathrm{CH_3}\\ \mathrm{C(CH_3)(C_2H_5){-}CO_2C_2H_5}\end{array}.$$

Lastly, these mono- and di-substituted aceto-acetic ethers, when heated alone, or better, with sodium ethylate, or with ethylic sodio-aceto-acetate, $C_6H_9NaO_3$, are resolved into the group C_2H_2O or $CH_2.CO$ (which, by polymerisation, yields dehydracetic acid, $C_8H_8O_4$), and substituted acetic ethers, that is to say, ethers of the higher fatty acids; *e.g.*,



$$CO{<}^{CH_3}_{CH(CH_3)-CO_2C_2H_5} = CH_3-CH_2-CO_2C_2H_5 + CH_2CO$$

Ethylic Methylaceto-acetate. Ethylic Methylacetate or Propionate.

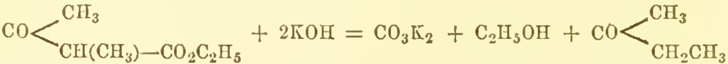


$$CO{<}^{CH_3}_{C(CH_3)_2-CO_2C_2H_5} = CH(CH_3)_2-CO_2C_2H_5 + CH_2CO$$

Ethylic Dimethyl-aceto-acetate. Ethylic Dimethyl-acetate or Isobutyrate.

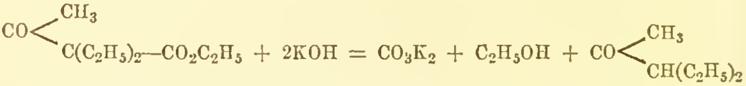
This reaction explains the direct production of the ethers of the higher fatty acids by the simultaneous action of sodium and alcoholic radicles on acetic ether (p. 271).

The substituted ethers of aceto-acetic acid, heated with aqueous alkalis, are decomposed in the same manner as ethylic aceto-acetate (p. 314), yielding various ketones; *e.g.*,



$$CO{<}^{CH_3}_{CH(CH_3)-CO_2C_2H_5} + 2KOH = CO_3K_2 + C_2H_5OH + CO{<}^{CH_3}_{CH_2CH_3}$$

Methyl-acetone.



$$CO{<}^{CH_3}_{C(C_2H_5)_2-CO_2C_2H_5} + 2KOH = CO_3K_2 + C_2H_5OH + CO{<}^{CH_3}_{CH(C_2H_5)_2}$$

Diethyl-acetone.

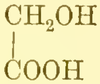
The following table exhibits the boiling points and specific gravities of these substituted acetacetic ethers, and their reactions with ferric chloride:

	Boiling Point.	Spec. Gravity.	Reaction with Ferric Chloride.
$CO{<}^{CH_3}_{CH(CH_3)-CO_2CH_3}$	177°	1·020 at 9°	Violet-red.
$CO{<}^{CH_3}_{CH(C_2H_5)-CO_2CH_3}$	190°	0·995 at 14°	Violet-red.
$CO{<}^{CH_3}_{CH(CH_3)-CO_2C_2H_5}$	186°		
$CO{<}^{CH_3}_{C(CH_3)_2--CO_2C_2H_5}$	184°	0·991 at 16°	
$CO{<}^{CH_3}_{CH(C_2H_5)-CO_2C_2H_5}$	195°	0·983 at 16°	Blue.
$CO{<}^{CH_3}_{C(C_2H_5)-CO_2C_2H_5}$	210°–212	0·974 at 0°	

Isopropylated acetacetic ethers are obtained by treating the acetacetic ethers with sodium and isopropyl iodide.

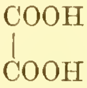
Diatomic Acids.

These acids contain two hydroxyl groups, and are monobasic or bibasic, according as one or both of these hydroxyls belongs to a carboxyl group, COOH; *e.g.*,



$$\begin{array}{l}CH_2OH\\ |\\ COOH\end{array}$$

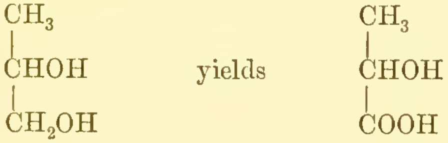
Glycollic acid.
1-basic.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array}$$

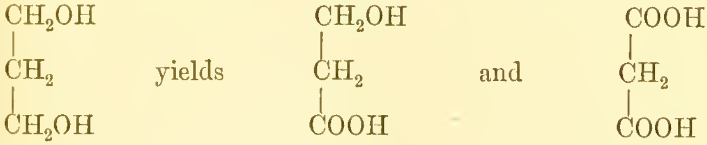
Oxalic acid.
2-basic.

Some of them are formed by oxidation (exchange of H_2 for O), from diatomic alcohols (glycols), containing the same number of carbon-atoms, those glycols which contain the group CH_2OH twice, yielding in this manner two diatomic acids, one mono- and the other bibasic, while those which contain this group only once yield only one acid, which is monobasic; thus:



$$\begin{array}{l}CH_3\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \quad \text{yields} \quad \begin{array}{l}CH_3\\ |\\ CHOH\\ |\\ COOH\end{array}$$

α-Propene glycol. α-Lactic acid.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2\\ |\\ CH_2OH\end{array} \quad \text{yields} \quad \begin{array}{l}CH_2OH\\ |\\ CH_2\\ |\\ COOH\end{array} \quad \text{and} \quad \begin{array}{l}COOH\\ |\\ CH_2\\ |\\ COOH\end{array}$$

β-Propene glycol. β-Lactic acid. Malonic acid.

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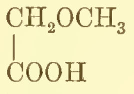
1. MONOBASIC ACIDS,

$$C_nH_{2n}O_3, \text{ or } C_nH_{2n}<^{OH}_{COOH}.$$

These acids are called lactic acids, after the most important member of the series, and oxy-fatty acids, because they may be derived from the acids $C_nH_{2n}O_2$ by substitution of OH for H; thus:

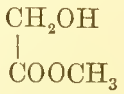
$CH_3.CO_2H$	$CH_2OH—CO_2H$
Acetic acid.	Oxyacetic acid.

They contain two hydroxyl groups, one alcoholic (connected with the radicle C_nH_{2n}), and having its hydrogen replaceable by monatomic alcohol-radicles, acid radicles, and alkali-metals; the other basic (connected with CO), and having its hydrogen replaceable by metals in general to form salts. Each of them can, therefore, form three ethers, containing monatomic alcohol-radicles, but only one series of metallic salts, except with the alkali-metals, with each of which they can form two salts. Of the ethers, one is acid and the other two are neutral; thus from glycollic acid, $CH_2OH.COOH$, are formed:



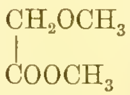
$$\begin{matrix} CH_2OCH_3 \\ | \\ COOH \end{matrix}$$

Methyl-glycollic acid.



$$\begin{matrix} CH_2OH \\ | \\ COOCH_3 \end{matrix}$$

Monomethylic glycollate.



$$\begin{matrix} CH_2OCH_3 \\ | \\ COOCH_3 \end{matrix}$$

Dimethylic glycollate.

The known members of the series are the following:

Carbonic acid, . . $CH_2O_3 = CO\Big<\begin{matrix} OH \\ OH \end{matrix}$

Glycollic or Oxyacetic acid, $C_2H_4O_3 = CH_2\Big<\begin{matrix} OH \\ CO_2H \end{matrix}$

Lactic or Oxypropionic acid, $C_3H_6O_3 = C_2H_4\Big<\begin{matrix} OH \\ CO_2H \end{matrix}$

Oxybutyric acid, . . $C_4H_8O_3 = C_3H_6\Big<\begin{matrix} OH \\ CO_2H \end{matrix}$

Oxyvaleric acid, . . $C_5H_{10}O_3 = C_4H_8\Big<\begin{matrix} OH \\ CO_2H \end{matrix}$

Oxycaproic acid, . . $C_6H_{12}O_3 = C_5H_{10}\Big<\begin{matrix} OH \\ CO_2H \end{matrix}$

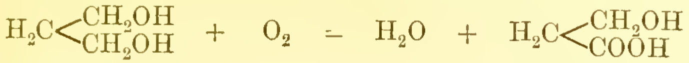
and others containing 7, 9, and 12 atoms of carbon.

All those acids of the series which contain more than two atoms of carbon admit of isomeric modifications. Of these some are analogous in structure to the primary or secondary alcohols, and are called *normal* or *iso*-acids, according to the structure of the alcohol-radicles contained in them. Others are analogous in structure to the tertiary alcohols, and are formed from oxalic acid or its ethers by a series of transformations to be presently explained.

They are all monobasic, as already observed, except carbonic acid, which is bibasic, its two hydroxyl groups being similarly related to the group CO. This acid will be considered by itself.

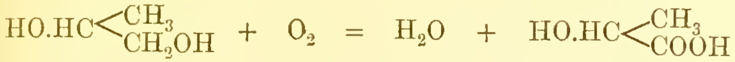
The *normal* and *iso-lactic acids* are formed by the following general processes:

1. By slow oxidation of the glycols in contact with platinum black, or by the action of dilute nitric acid; *e.g.*,



$$H_2C{<}\begin{matrix}CH_2OH\\CH_2OH\end{matrix} + O_2 = H_2O + H_2C{<}\begin{matrix}CH_2OH\\COOH\end{matrix}$$

β-Propene glycol. β-Lactic acid.



$$HO.HC{<}\begin{matrix}CH_3\\CH_2OH\end{matrix} + O_2 = H_2O + HO.HC{<}\begin{matrix}CH_3\\COOH\end{matrix}$$

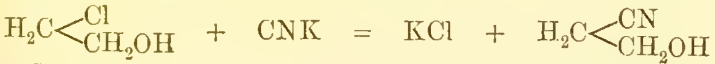
α-Propene glycol. α-Lactic acid.

2. By the action of moist silver oxide on the monochlorinated or monobrominated derivatives of the fatty acids (p. 275); *e.g.*,

$$CH_2Cl—CO_2H + AgOH = AgCl + CH_2OH—CO_2H$$

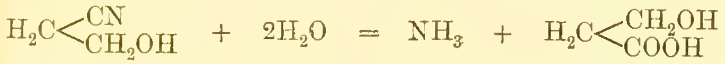
Chloracetic acid. Glycollic acid.

3. From the glycolic chlorhydrins (p. 167), by converting them into cyanides by the action of potassium cyanide, and boiling the resulting cyanides with alkalis or acids:



$$H_2C{<}\begin{matrix}Cl\\CH_2OH\end{matrix} + CNK = KCl + H_2C{<}\begin{matrix}CN\\CH_2OH\end{matrix}$$

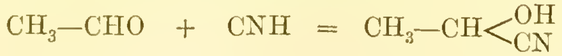
Chlorhydrin. Cyanhydrin.



$$H_2C{<}\begin{matrix}CN\\CH_2OH\end{matrix} + 2H_2O = NH_3 + H_2C{<}\begin{matrix}CH_2OH\\COOH\end{matrix}$$

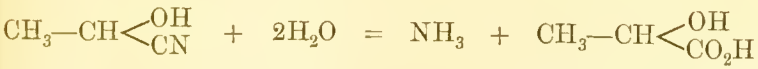
Cyanhydrin. β-Lactic acid.

4. By heating an aldehyde or a ketone with hydrocyanic and hydrochloric acid, whereby a cyanhydrin is produced, and treating this compound with acids or alkalis as above:



$$CH_3—CHO + CNH = CH_3—CH{<}\begin{matrix}OH\\CN\end{matrix}$$

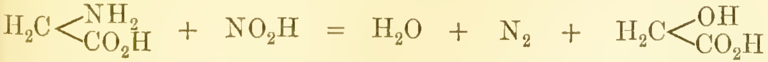
Aldehyde.



$$CH_3—CH{<}\begin{matrix}OH\\CN\end{matrix} + 2H_2O = NH_3 + CH_3—CH{<}\begin{matrix}OH\\CO_2H\end{matrix}$$

α-Lactic acid.

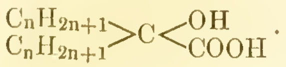
5. By the action of nitrous acid on the amidated derivatives of the fatty acids:



$$H_2C{<}\begin{matrix}NH_2\\CO_2H\end{matrix} + NO_2H = H_2O + N_2 + H_2C{<}\begin{matrix}OH\\CO_2H\end{matrix}$$

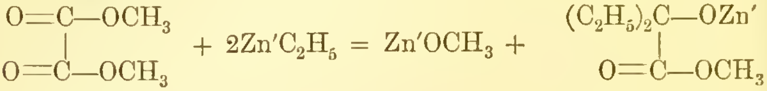
Amidacetic acid. Glycollic acid.

The *tertiary lactic acids* are represented by the general formula:



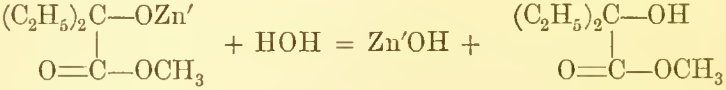
$$\begin{matrix}C_nH_{2n+1}\\C_nH_{2n+1}\end{matrix}{>}C{<}\begin{matrix}OH\\COOH\end{matrix}.$$

They are obtained in the form of ethers by the action of the zinc-compound of an alcohol-radicle, C_nH_{2n+1}, on a neutral ether of oxalic acid containing a radicle of the same series, such as diethylic oxalate. The reaction consists in the replacement of an atom of oxygen in the oxalic ether by two equivalents of alcohol-radicle, and the simultaneous replacement of an equivalent of ethyl, methyl, &c., in the oxalic ether by an equivalent* of zinc, whereby an ether of zinc-diethoxalic acid, &c., is produced, which by certain obvious transformations may be converted into the required acid; thus:



$$\begin{array}{l} O{=}C{-}OCH_3 \\ \quad | \\ O{=}C{-}OCH_3 \end{array} + 2Zn'C_2H_5 = Zn'OCH_3 + \begin{array}{l} (C_2H_5)_2C{-}OZn' \\ \qquad | \\ O{=}C{-}OCH_3 \end{array}$$

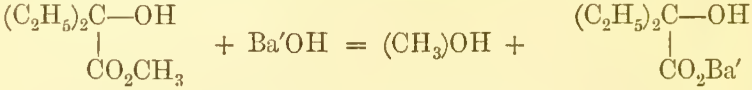
Dimethylic oxalate. Methylic zinco-diethoxalate.



$$\begin{array}{l} (C_2H_5)_2C{-}OZn' \\ \qquad | \\ O{=}C{-}OCH_3 \end{array} + HOH = Zn'OH + \begin{array}{l} (C_2H_5)_2C{-}OH \\ \qquad | \\ O{=}C{-}OCH_3 \end{array}$$

Methyl zinco-diethoxalate. Methylic diethoxalate.

The methylic diethoxalate is easily decomposed by baryta-water, yielding methyl alcohol and barium diethoxalate:



$$\begin{array}{l} (C_2H_5)_2C{-}OH \\ \qquad | \\ \quad CO_2CH_3 \end{array} + Ba'OH = (CH_3)OH + \begin{array}{l} (C_2H_5)_2C{-}OH \\ \qquad | \\ \quad CO_2Ba' \end{array}$$

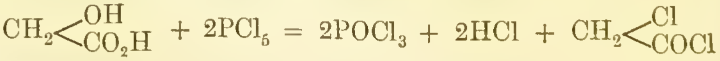
and this salt decomposed by sulphuric acid yields diethoxalic acid, $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}{>}C{<}\begin{matrix} OH \\ CO_2H \end{matrix}$, isomeric with leucic acid.

In the first stage of the process, it is found better to use a mixture of ethyl iodide with metallic zinc, which produces zinc ethide, instead of the latter compound previously prepared. The other tertiary lactic acids are prepared in a similar manner.

Reactions.—1. All the acids of the series, $C_nH_{2n}O_3$, are reduced by *hydriodic acid* to the corresponding monatomic acids, $C_nH_{2n}O_2$, *e.g.*, lactic to propionic acid:

$$C_3H_6O_3 + 2HI = H_2O + I_2 + C_3H_6O_2.$$

By the action of *phosphorus pentachloride*, both their hydroxyl groups are replaced by chlorine; thus glycollic acid yields glycollyl chloride, or chloracetyl chloride, $CH_2Cl.CO.Cl$:



$$CH_2{<}\begin{matrix} OH \\ CO_2H \end{matrix} + 2PCl_5 = 2POCl_3 + 2HCl + CH_2{<}\begin{matrix} Cl \\ COCl \end{matrix}$$

Glycollic acid. Glycollyl chloride.

The chlorine in the group COCl of the resulting chlorides is easily attacked by water and alcohols, forming acids or ethers: chloracetyl chloride, for example, yielding chloracetic acid, $CH_2Cl.CO.OH$, or its ethers.

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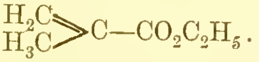
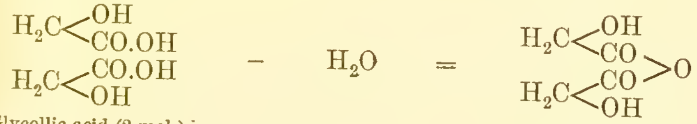
* To simplify the equations, the *equivalent* of zinc ($Zn' = 32{\cdot}5$) is used instead of the atom (65).

2. The ethers of the tertiary lactic acids, when treated with PCl_3 or P_2O_5, are converted (by abstraction of H_2O) into ethers of the acrylic series (p. 305), *e.g.*, ethylic dimethoxalate, $(CH_3)_2COH—CO_2C_2H_5$, into ethylic methylacrylate,



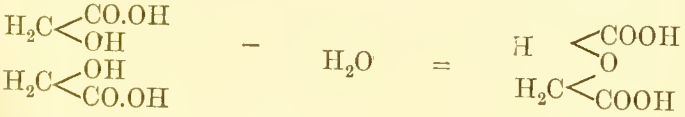
$$\begin{matrix}H_2C\\H_3C\end{matrix}{>}C—CO_2C_2H_5 .$$

3. The isolactic acids, when deprived of the elements of water by the action of heat or otherwise, are converted into anhydrides, which may be of three kinds. If the elements of 1 mol. H_2O, are removed partly from one and partly from another molecule of the acid, and the two residues unite, the result is an anhydride of the first order, differing in constitution and properties according as the two hydrogen-atoms are taken from the carboxyl-groups, or from the alcoholic hydroxyls; in the former case, the product is an acid anhydride; in the latter, an alcoholic anhydride, or anhydro-acid; thus:



$$\begin{matrix}H_2C{<}\begin{matrix}OH\\CO.OH\end{matrix}\\H_2C{<}\begin{matrix}CO.OH\\OH\end{matrix}\end{matrix} \quad - \quad H_2O \quad = \quad \begin{matrix}H_2C{<}\begin{matrix}OH\\CO\end{matrix}\\H_2C{<}\begin{matrix}CO\\OH\end{matrix}\end{matrix}{>}O$$

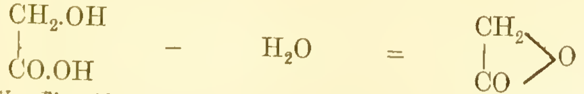
Glycollic acid (2 mol.); Glycollic anhydride.



$$\begin{matrix}H_2C{<}\begin{matrix}CO.OH\\OH\end{matrix}\\H_2C{<}\begin{matrix}OH\\CO.OH\end{matrix}\end{matrix} \quad - \quad H_2O \quad = \quad \begin{matrix}H \;{<}\begin{matrix}COOH\\O\end{matrix}\\H_2C{<}COOH\end{matrix}$$

Diglycollic acid.

If, on the other hand, one molecule of water is removed from one molecule of the acid, the remainder constitutes an anhydride of the second order; *e.g.*:



$$\begin{matrix}CH_2.OH\\|\\CO.OH\end{matrix} \quad - \quad H_2O \quad = \quad \begin{matrix}CH_2\\|\\CO\end{matrix}{>}O$$

Glycollic acid. Glycollide.

Glycollic Acid, $C_2H_4O_3 = CH_2{<}\begin{matrix}OH\\CO_2H\end{matrix}$.—This acid is produced in a variety of reactions, some of which have been already mentioned, viz., the oxidation of glycol by contact with platinum black or by treatment with dilute nitric acid; the decomposition of amidacetic acid (glycocine) by nitrous acid; the action of water or alkalis on bromacetic and chloracetic acid, or their salts (p. 275), *e.g.*, by boiling silver bromacetate with water:

$$C_2H_2BrAgO_2 + H_2O = AgBr + C_2H_4O_3 .$$

It is also produced: α. By the action of alkalis on glyoxal and glyoxylic acid:

$$\underset{\text{Glyoxal.}}{C_2H_2O_2} + H_2O = \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

$$\underset{\text{Glyoxyllic acid.}}{2C_2H_2O_3} + H_2O = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

β. Together with glyoxal, glyoxylic acid, and other products, by the action of nitric acid upon alcohol.

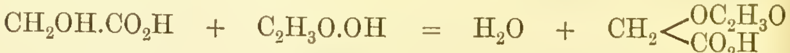
γ. By the action of nascent hydrogen (evolved by zinc and sulphuric acid) upon oxalic acid :

$$C_2H_2O_4 + 2H_2 = H_2O + C_2H_4O_3 \cdot$$

Glycollic acid differs somewhat in its properties, according to the manner in which it is prepared, being sometimes syrupy and uncrystallisable, sometimes separating from its solution in ether in large regular crystals. It has a very sour taste, dissolves easily in water, alcohol, and ether ; melts at 78° or 79° ; begins to boil at 100° ; decomposes when heated to above 150°. All the glycollates are more or less soluble and crystallisable.

The *calcium salt*, $(C_2H_3O_3)_2Ca + 2H_2O$, is slightly soluble in cold water, and crystallises in needles. The *silver salt*, $C_2H_3O_3Ag + \frac{1}{2}H_2O$, is also sparingly soluble. The *ethylic ether*, $C_2H_3O_3.C_2H_5$, is a liquid having a specific gravity of 1·03, and boiling at 150°.

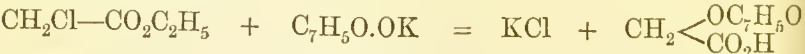
Acid and Alcoholic Derivatives of Glycollic Acid.—The alcoholic hydrogen of glycollic acid may be replaced either by acid or by alcoholic radicles. The acid derivatives are formed : α. By heating glycollic acid with monatomic acids :



$$CH_2OH.CO_2H + C_2H_3O.OH = H_2O + CH_2<\begin{array}{l}OC_2H_3O\\CO_2H\end{array}$$

Glycollic acid. Acetic acid. Acetoglycollic acid.

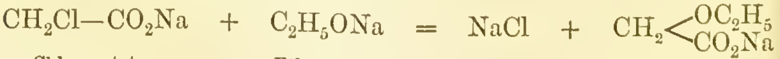
β. By the action of the alkali-salts of monatomic acids on ethylic monochloracetate :



$$CH_2Cl{-}CO_2C_2H_5 + C_7H_5O.OK = KCl + CH_2<\begin{array}{l}OC_7H_5O\\CO_2H\end{array}$$

Ethylic chloracetate. Potassium Benzoate. Benzoglycollic acid.

The alcoholic derivatives are formed by the action of sodium alcoholates on chloracetic acid :



$$CH_2Cl{-}CO_2Na + C_2H_5ONa = NaCl + CH_2<\begin{array}{l}OC_2H_5\\CO_2Na\end{array}$$

Chloracetate. Ethylate. Ethyl-glycollate.

Methyl-glycollic acid, $CH_2OCH_3.CO_2H$, boils at 198° ; *ethyl-glycollic acid*, $CH_2OC_2H_5.CO_2H$, at 206°. Both are permanent in the air, and are not decomposed by boiling with alkalis.

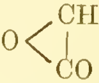
Anhydrides.—Diglycollic acid, $C_4H_6O_5 = 2C_2H_4O_3 - H_2O = O<\begin{array}{l}CH_2{-}COOH\\CH_2{-}COOH\end{array}$, also called *Paramalic acid.*—This acid, isomeric with malic acid, and related to glycollic acid in the same manner as diethenic alcohol to glycol, is produced by the dehydration of glycollic acid, and by the oxidation of diethenic or triethenic alcohol. It is also formed in the preparation of glycollic acid by heating sodium chloracetate with caustic soda, which in fact is the process by which it was first obtained :

$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + 2NaHO = NaCl + H_2O + \underset{\text{Sodium glycollate.}}{C_2H_3NaO_3}$$

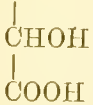
$$\underset{\text{Chloracetic acid}}{C_2H_3ClO_2} + \underset{\text{Sodium glycollate.}}{C_2H_3NaO_3} = NaCl + \underset{\text{Diglycollic acid.}}{C_4H_6O_5}$$

Diglycollic acid crystallises in large rhombic prisms, melting at 150°, and distilling with slight decomposition at 250° ; easily soluble in water and in alcohol ; not decomposed by boiling with alkalis. It is bibasic, forming with univalent metals, acid salts containing $C_4H_5M'O_5$, and normal salts, $C_4H_4M_2O_5$; with bivalent metals it forms only normal salts, $C_4H_4M''O_5$. The *calcium salt* is very soluble.

Glycollic Anhydride, $C_4H_6O_5 = O{<}\begin{matrix}CO—CH_2OH\\CO—CH_2OH\end{matrix}$, obtained by exposing the acid for a few days to the vapours of sulphuric anhydride, is a lustreless powder, melting at 128°–130° ; insoluble in alcohol, ether, and cold water ; boiling water reconverts it into glycollic acid and dissolves it.

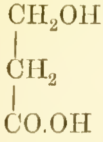
Glycollide, $C_2H_2O_2 = $  $O{<}\begin{matrix}CH_2\\|\\CO\end{matrix}$, is formed by heating glycollic acid to 150°. It is a white, amorphous powder, melting at 180°, insoluble in cold water, reconverted into glycollic acid by boiling with water. Heated with ammonia it yields glycollamide, $CH_2OH—CONH_2$

Lactic or **Oxypropionic Acids**, $C_3H_6O_3 = C_2H_4{<}\begin{matrix}OH\\CO.OH\end{matrix}$ —Of these acids there are two isomeric modifications, viz. :



$$\begin{matrix}CH_3\\|\\CHOH\\|\\COOH\end{matrix}$$

-Lactic or
Ethidene-lactic acid.

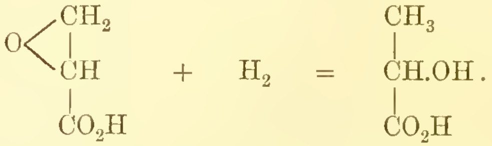


$$\begin{matrix}CH_2OH\\|\\CH_2\\|\\CO.OH\end{matrix}$$

β-Lactic or
Ethene-lactic acid.

1. **Ethidene-lactic** or **Isolactic Acid**, $HOHC{<}\begin{matrix}CH_3\\CO_2H\end{matrix}$, is the ordinary lactic acid produced by a peculiar fermentation of sugar and other carbohydrates, hence called *fermentation-lactic acid*

It is also produced by the first, second, fourth, and fifth of the general reactions already mentioned (p. 319), viz., by oxidation of α-propene-glycol; by the action of moist silver oxide on α-chloropropionic acid; by the action of hydrocyanic and hydrochloric acid on aldehyde; and by that of nitrous acid on α-amidopropionic acid (alanine); and lastly, by the action of nascent hydrogen on pyruvic acid:



Preparation of ordinary Lactic Acid by Fermentation.—Various kinds of sugar and dextrin, when subjected to the action of particular ferments, are converted into lactic acid, the change consisting in a resolution of the molecule, preceded in some cases by the assumption of the elements of water:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2C_3H_6O_3}$$

$$\underset{\text{Milk sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Lactic acid.}}{4C_3H_6O_3}$$

This lactous fermentation requires a temperature between 20° and 40° C. (58° and 104° F.), and the presence of water and certain ferments—viz., albuminous substances in a peculiar state of decomposition, such as casein, glutin, or animal membranes, especially the coating of the stomach of the calf (rennet), or of the dog, or bladder. According to Pasteur and others, it depends upon the presence of a peculiar fungus, *Penicillium glaucum* (p. 130). The following is a good method for preparing the acid in considerable quantity:—2 gallons of milk are mixed with 6 pounds of raw sugar, 12 pints of water, 8 ounces of putrid cheese, and 4 pounds of chalk, which should be mixed up to a creamy consistence with some of the liquid. This mixture is exposed in a loosely covered jar to a temperature of about 86° F. (30° C.), with occasional stirring. The use of the chalk is to neutralise the lactic acid, which would otherwise coagulate the casein, render it insoluble, and thereby put a stop to the process. At the end of two or three weeks it will be found converted into a semi-solid mass of calcium lactate, which may be drained, pressed, and purified by re-crystallisation from water. The lactate may be decomposed by the necessary quantity of pure oxalic acid, the filtered liquor neutralised with zinc carbonate, and, after a second filtration, evaporated until the zinc-salt crystallises out in cooling. If, in the first part of the process, the solid calcium lactate be not removed at the proper time from the fermenting liquid, it will gradually redissolve and disappear, being converted into soluble butyrate (p. 291). An important modification of this process consists in employing commercial zinc-white instead of powdered chalk, which yields at once difficultly soluble zinc lactate, easily purified by recrystallisation. The zinc lactate may, lastly, be redissolved in water and decomposed by sulphuretted hydrogen, in order to obtain the free acid. Together with the lactic acid a certain quantity of mannite is invariably formed. This is separated by agitating the concentrated aqueous solution with ether, in which the lactic acid alone is soluble.

Lactic acid may be extracted from a great variety of liquids containing decomposing organic matter, as *sauerkraut*, a preparation of white cabbage, the sour liquor of the starch-maker, &c.

Solution of lactic acid may be concentrated in the vacuum of the air-pump, over a surface of oil of vitriol, until it appears as a colourless, syrupy liquid, of sp. gr. 1·215. It has an intensely sour taste and acid reaction: it is hygroscopic, and very soluble in water, alcohol, and ether.

By prolonged evaporation over sulphuric acid it is partly resolved in water and anhydride, and by distillation it splits up into lactide, $C_3H_4O_2$, aldehyde, carbon monoxide, and water.

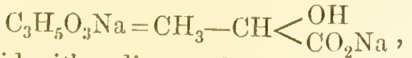
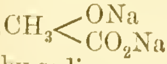
By oxidation with chromic acid mixture lactic acid yields formic and acetic acids. Boiled with dilute *nitric acid*, or with dioxide of lead or barium, it is converted into oxalic acid. Distilled with dilute sulphuric acid and dioxide of lead or manganese, it yields a large quantity of aldehyde, together with carbon dioxide. Hydriodic acid, or a mixture of phosphorus tetriodide and water, reduces it to propionic acid, with liberation of iodine:

$$C_3H_6O_3 + 2HI = C_3H_6O_2 + H_2O + I_2.$$

By heating with hydrobromic acid it is converted into α-bromopropionic acid:

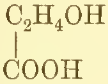
$$CH_3—CH(OH)—CO_2H + HBr = H_2O + CH_3—CHBr—CO_2H.$$

Lactates.—The best defined of these salts are represented by the formulæ, $M'C_3H_5O_3$ and $M''(C_3H_5O_3)_2$. Barium and calcium also form acid lactates, *e.g.*, $Ca(C_3H_5O_3)_2.2C_3H_6O_3$. The lactates are, for the most part, sparingly soluble in cold water, and effloresce rapidly from their solutions: they are all insoluble in ether. When heated with excess of strong sulphuric acid, they give off a large quantity of pure carbon monoxide.

Sodium lactate,  $C_3H_5O_3Na = CH_3—CH{<}\substack{OH \\ CO_2Na}$, obtained by neutralising the acid with sodium carbonate, is an amorphous mass, which, when heated with metallic sodium is converted into disodic lactate,  $CH_3{<}\substack{ONa \\ CO_2Na}$, the alcoholic hydrogen being likewise replaced by sodium.

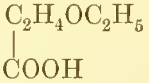
Calcium lactate, $(C_3H_5O_3)_2Ca + 5H_2O$, is obtained in the fermentation process above described, or by boiling aqueous lactic acid with calcium carbonate. It dissolves in 9·5 parts of water at ordinary temperatures.—*Zinc lactate*, $(C_3H_5O_3)_2Zn + 3H_2O$., gives off its water quickly at 100°, dissolves in 6 parts of boiling water, in 5·8 parts of cold water, and is nearly insoluble in alcohol.—*Ferrous lactate* is precipitated in small yellowish needles on mixing ammonium lactate with ferrous chloride or sulphate.—*Ferric lactate* is a brown deliquescent mass.

Lactic Ethers.—Lactic acid, like the other members of the group, can form three different ethers containing the same univalent alcohol-radicle, according as the alcoholic or the basic hydrogen-atom, or both, are replaced; thus:



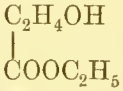
$$\begin{array}{l} C_2H_4OH \\ | \\ COOH \end{array}$$

Lactic acid.



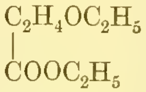
$$\begin{array}{l} C_2H_4OC_2H_5 \\ | \\ COOH \end{array}$$

Ethyl-lactic acid.



$$\begin{array}{l} C_2H_4OH \\ | \\ COOC_2H_5 \end{array}$$

Monethylic lactate.



$$\begin{array}{l} C_2H_4OC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

Diethylic lactate, or ethylic ethyl-lactate.

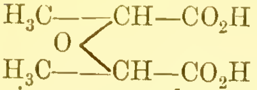
Monethylic lactate, $C_3H_5O_3.C_2H_5$, is produced by distilling potassium or sodium lactate with potassium ethylsulphate. It is a syrupy liquid, boiling at 176°. Potassium dissolves in it, with evolution of hydrogen, forming ethylic potassiolactate, $\begin{array}{l} C_2H_4OK \\ | \\ COOC_2H_5 \end{array}$.—*Ethyl-lactic acid*, $C_2H_4(OC_2H_5)—CO_2H$, is obtained as a potassium or calcium salt by decomposing diethylic lactate with potash or milk of lime. When separated from these salts by sulphuric acid, it forms a viscid liquid, boiling with partial decomposition between 195° and 198°.—*Diethylic lactate*, $C_2H_4(OC_2H_5)—CO_2C_2H_5$, is produced by the action of ethyl-iodide on ethyl potassiolactate, and by that of sodium ethylate on ethyl chloropropionate:

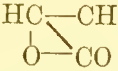
$$\underset{\text{Ethyl chloropropionate.}}{C_2H_4Cl—COC_2H_5} + \underset{\text{Sodium ethylate.}}{NaOC_2H_5} = NaCl + \underset{\text{Diethylic lactate.}}{C_2H_4(OC_2H_5)—CO_2C_2H_5}$$

Methyl-lactic acid, $C_3H_5(CH_3)O_3$, and its zinc and silver salts have also been obtained.

The alcoholic hydrogen of lactic acid may also be replaced by acid radicles, forming such compounds as acetolactic acid, $C_2H_4{<}\begin{array}{l} OC_2H_3O \\ CO_2H \end{array}$.

Lactyl Chloride, $C_3H_4OCl_2$, or *α-Chloropropionyl Chloride*, $C_2H_4Cl—COCl$, is obtained, together with phosphorus oxychloride, by gently heating a mixture of calcium lactate with phosphorus pentachloride. It is a colourless liquid, boiling above 100°, and decomposed by water, forming hydrochloric and chloropropionic acids. With alcohol it forms ethylic α-chloropropionate. By heating with alkalis it is converted into lactic acid.

Lactic Anhydrides.—1. Dilactic acid, $C_6H_{10}O_5 = 2C_3H_6O_3 - H_2O =$  $\mathrm{O}\left\langle\begin{matrix}\mathrm{H_3C{-}CH{-}CO_2H}\\ \mathrm{H_3C{-}CH{-}CO_2H}\end{matrix}\right.$, formed by heating lactic acid to 130°–200°, is an amorphous mass, very bitter, and nearly insoluble in water, but reconverted into lactic acid by prolonged boiling with water.

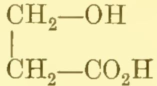
2. Lactide, $C_3H_4O_2 =$  $\begin{matrix}\mathrm{HC{-}CH_3}\\ \mathrm{O{-}CO}\end{matrix}$, the second anhydride of lactic acid, is obtained by distillation of lactic or dilactic acid, and may be obtained pure by evaporating the distillate, washing the residue with cold alcohol, and crystallising it from hot alcohol. Lactide thus purified crystallises in rhombic plates which melt at 107° : it dissolves gradually in water.

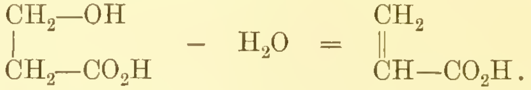
Paralactic or *Sarcolactic acid*, is a modification of lactic acid, existing in the animal organism, especially in muscular flesh, from which it may be extracted by cold water or dilute alcohol. It is most easily prepared from Liebig's extract of meat. It agrees in all its reactions with fermentation lactic acid, and must therefore have the same chemical structure—that is to say, it must be an ethidene-lactic acid—but it differs from ordinary lactic acid in its relation to polarised light, inasmuch as it turns the plane of polarisation to the left, whereas ordinary lactic acid is optically inactive. Hence it is inferred that the two modifications, though chemically identical, differ from one another in physical structure ; in other words, that the difference between them consists, not in the arrangement of the atoms within the molecules, but in the arrangement or modification of the molecules amongst themselves. There are other cases of difference in physical character coexisting with chemical identity, which are attributed to a similar difference of physical structure, as in the several modifications of turpentine oil.

Some of the paralactates differ from the ordinary lactates in solubility and other characters ; thus :

	Lactate.	Paralactate.
Calcium Salts.	$(C_3H_5O_3)_2Ca + 5H_2O$; nodular groups of needles, soluble in 9·5 parts of cold water.	$+ 4H_2O$; soluble in 12 parts of cold water.
Zinc Salts.	$(C_3H_5O_3)_2Zn + 3H_2O$; slender needles, soluble in 58 parts of cold water.	$+ 2H_2O$; thick shining prisms, soluble in 17 parts of water at 15°.

Paralactic acid heated to 130°, yields dilactic acid, convertible by water into ordinary lactic acid.

2. **Ethene-lactic** or **Hydracrylic Acid,**  $\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}CO_2H \end{array}$.—This acid is produced by heating β-iodopropionic acid with moist silver oxide; $CH_2I\text{—}CH_2\text{—}CO_2H + AgOH = AgI + CH_2OH\text{—}CH_2\text{—}CO_2H$. It is a thick uncrystallisable syrup, which, when heated alone or boiled with sulphuric acid diluted with an equal weight of water, is converted by dehydration into acrylic acid:



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}CO_2H \end{array} - H_2O = \begin{array}{l} CH_2 \\ \| \\ CH\text{—}CO_2H. \end{array}$$

By heating with hydriodic acid, it is reconverted into β-iodopropionic acid; by oxidation with chromic acid mixture, or nitric acid, it yields oxalic acid and carbon dioxide. When heated with silver oxide it is converted into carbacetoxylic acid, $C_3H_4O_4$.

The metallic hydracrylates are crystallisable. The *sodium salt*, $C_3H_5O_3Na$, crystallises in flat prisms, which melt without loss of weight at 142°–148°, but give off water at 150°, leaving sodium acrylate, $C_3H_3O_2Na$. The *calcium salt*, $(C_3H_5O_3)_2Ca + 2H_2O$, forms large rhombic prisms, which give off their water of crystallisation at 100°. The dehydrated salt unites without alteration at 140°–145°, but at 190° it gives off water, and is converted into acrylate, $(C_3H_5O_3)_2Ca - 2H_2O = (C_3H_3O_2)_2Ca$. The *zinc salt*, $(C_3H_5O_3)_2Zn + 4H_2O$, crystallises from a moderately strong solution in large shining prisms, soluble in an equal weight of water at 15°.*

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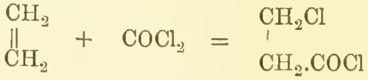
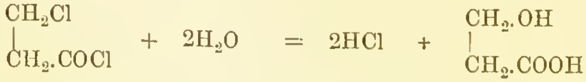
* According to Wislicenus (Liebig's *Annalen*, clxv. 6), hydracrylic acid prepared from β-iodopropionic acid is not identical with ethene-lactic acid prepared by combining ethene with carbonyl chloride (phosgene), and decomposing the resulting compound with water:

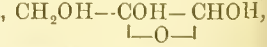


$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + COCl_2 = \begin{array}{l} CH_2Cl \\ | \\ CH_2.COCl \end{array}$$

and



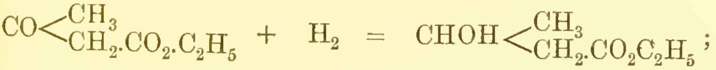
$$\begin{array}{l} CH_2Cl \\ | \\ CH_2.COCl \end{array} + 2H_2O = 2HCl + \begin{array}{l} CH_2.OH \\ | \\ CH_2.COOH \end{array}$$

The ethene-lactic acid thus obtained is converted by oxidation with chromic acid or nitric acid into malonic acid, $COOH\text{—}CH_2\text{—}COOH$, whereas hydracrylic acid, as above stated, is resolved thereby into oxalic acid and carbon dioxide. Moreover, the salts of hydracrylic acid are crystalline, whereas those of ethene-lactic acid are amorphous. To account for these differences, Wislicenus assigns to hydracrylic acid the formula,  $\underbrace{CH_2OH\text{—}COH\text{—}CHOH}_{\text{—O—}}$, and corresponding formulæ to β-iodopropionic acid and acrylic acid. These formulæ, however, are somewhat improbable, as they do not contain the group COOH; moreover, the formation of ethene-lactic acid from ethene in the manner described by Wislicenus does not appear to be well established. (See Watts's Dictionary of Chemistry, 2nd Suppl., 718).

Oxybutyric Acids, $C_4H_8O_3 = C_3H_6<\substack{OH\\CO_2H}$.—Five of these acids are theoretically possible, and four are known.

1. *α-Oxybutyric acid,* $CH_3—CH_2—CHOH—CO_2H$, is formed by heating α-bromobutyric acid with moist silver oxide, or with aqueous potash. It is crystalline, very deliquescent, and melts at 43°-44°. Its salts are crystalline, the zinc-salt, $(C_4H_7O_3)_2Zn$, forming white laminæ, slightly soluble in cold water.

2. *β-Oxybutyric acid,* $CH_3—CHOH—CH_2—CO_2H$, is produced by boiling β-bromobutyric acid with silver oxide: by the action of sodium amalagam on ethylic aceto-acetate:



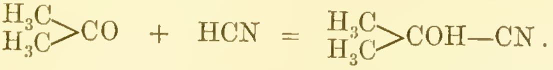
$$CO<\substack{CH_3\\CH_2.CO_2.C_2H_5} + H_2 = CHOH<\substack{CH_3\\CH_2.CO_2C_2H_5};$$

by the oxidation of aldol, $CH_3—CHOH—CH_2—CHO$ (p. 258); and apparently also by heating propene-chlorhydrin, $CH_3.CHOH.CH_2Cl$, with potassium cyanide, whereby it is converted into the corresponding cyanhydrin, and saponifying the latter with potash. The free acid is an uncrystallisable syrup; the calcium salt, $(C_4H_7O_3)_2Ca$, crystallises with difficulty. The acid obtained from propene-chlorhydrin is resolved by distillation into water and solid crotonic acid, $CH_3—CH{=}CH—CO_2H$.

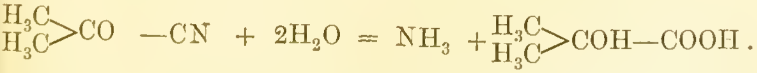
3. *γ-Oxybutyric acid,* or *Normal Oxybutyric acid,* $CH_2OH—CH_2—CH_2—CO_2H$, is prepared from succinic acid, $CHO—CH_2—CH_2—CHO$.

4. *Oxyisobutyric acid,* $\substack{H_3C\\H_3C}>COH—CO_2H$, is produced:

α. By the action of hydrocyanic and hydrochloric acids on acetone; hence called acetonic acid:



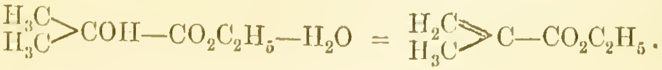
$$\substack{H_3C\\H_3C}>CO + HCN = \substack{H_3C\\H_3C}>COH—CN.$$



$$\substack{H_3C\\H_3C}>CO—CN + 2H_2O = NH_3 + \substack{H_3C\\H_3C}>COH—COOH.$$

β. From ethyl oxalate by the action of methyl iodide and zinc (p. 305): hence called dimethyloxalic acid. γ. From bromisobutyric acid, $(CH_3)_2CBr—CO_2H$, by boiling with baryta-water. δ. By oxidation of isopentene glycol (p. 177).

Oxyisobutyric acid crystallises in slender prisms, soluble in water and in ether. It sublimes at 50°, melts at 79°, and distils at 212°. Its ethylic ether, treated with phosphorus trichloride, is converted into ethylic methylacrylate:



$$\substack{H_3C\\H_3C}>COH—CO_2C_2H_5—H_2O = \substack{H_2C\\H_3C}>C—CO_2C_2H_5.$$

By oxidation with chromic acid mixture, oxyisobutyric acid is resolved into carbon dioxide and acetone. Its *barium salt*, $(C_4H_7O_3)_2Ba$, forms shining needles, easily soluble in water. The *zinc salt*, $(C_4H_7O_3)_2Zn + 2H_2O$, crystallises in shining six-sided prisms or tables, sparingly soluble in cold water.

Oxyvaleric Acids, $C_5H_{10}O_3 = C_4H_8{<}\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$.—1. *α-Oxyisovaleric* or *Isopropyl-hydroxalic acid*, $\begin{smallmatrix}H_3C\\ H_3C\end{smallmatrix}{>}CH{-}HC{<}\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$. —This acid, prepared from the corresponding bromovaleric acid, forms large tabular crystals, easily soluble in water, melting at 80°, and volatilising at about 100°. When oxidised with chromic acid mixture, it yields carbon dioxide and isobutyric acid.

The ethylic ether of this acid is formed, together with that of oxyisocaprylic acid (*infra*), by the action of isopropyl iodide and zinc on ethylic oxalate, and may be obtained by evaporating the potash-solution used in the preparation of oxyisocaprylic acid, acidulating with sulphuric acid, agitating with ether and evaporating the ethereal solution. The oxyisovaleric acid then remains as a thick liquid which solidifies in the exsiccator.

2. *Methyl-ethyloxalic acid*, $\begin{smallmatrix}H_3C\\ H_5C_2\end{smallmatrix}{>}C{<}\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$, obtained by the action of a mixture of methylic and ethylic iodide and zinc on ethyl oxalate, forms white crystals, easily soluble in water, and melting at 63°. Its ethylic ether is soluble in water, boils at 165°, and is converted by phosphorus trichloride into the ethylic ether of methyl-crotonic acid.

Oxycaproic Acids, $C_6H_{12}O_3 = C_6H_{10}{<}\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$.—1. *Leucic acid*, propably *α-Oxycaproic acid*, $C_4H_9{-}CHOH{-}CO_2H$, is produced by the action of nitrous acid on leucine or amidocaproic acid (see AMIDES). It forms needles or monoclinic prisms, soluble in water, alcohol, and ether, melting at about 73°, and volatilising at 100°. When heated for some time at that temperature, it gives off water, and leaves a syrupy oxide or anhydride. It forms crystallisable salts analogous to the lactates; the zinc salt crystallises in shining scales.

2. *Diethyloxalic acid*, $(C_2H_5)_2C{<}\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$, formed by the action of ethyl iodide and zinc on ethylic oxalate, is crystalline, easily soluble in water and ether, melts at 74·5°, and sublimes at about 50°. Its methylic ether boils at 165°, and is converted by the action of phosphorus trichloride into methylic ethylcrotonate (p. 310). The free acid, oxidised by chromic acid mixture, yields diethylketone, $CO(C_2H_5)$.

Oxyisoheptoic or **Amylhydroxalic Acid**, $C_7H_{14}O_3 = \begin{smallmatrix}C_5H_{11}\\ H\end{smallmatrix}>C<\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$, and **Diamyl-oxalic Acid**, $C_{12}H_{24}O_3 = \begin{smallmatrix}C_5H_{11}\\ C_5H_{11}\end{smallmatrix}>C<\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$, are formed by the action of zinc and isopentyl iodide on ethylic oxalate. The former is a thick syrup ; its ethylic ether boils at 203°. The latter crystallises in silky needles, is nearly insoluble in water, and melts at 122°. Its ethylic ether boils at 262°.

Oxyisocaprylic or **Di-isopropyloxalic Acid**, $C_8H_{16}O_3 = (C_3H_7)_2C<\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$, obtained by the action of isopropyl iodide and zinc on ethylic oxalate, forms slender needles, slightly soluble in water, melts at 110°–111°, and sublimes at a moderate heat.

Carbonic Acid, $CH_2O_3 = CO<\begin{smallmatrix}OH\\ OH\end{smallmatrix}$.—This acid belongs to the lactic series, so far as its constitution is concerned, being derived from the unknown methene glycol, $CH_2<\begin{smallmatrix}OH\\ OH\end{smallmatrix}$, by substitution of O for H_2 ; but it differs from all the other acids of the series in being bibasic, both the hydroxyl groups contained in it being immediately connected with an atom of oxygen, so that either of the hydrogen-atoms may be regarded as belonging to the group CO_2H.

Carbonic acid itself, or hydrogen carbonate, is not known, inasmuch as when a metallic carbonate is decomposed by a stronger acid, the hydrogen carbonate, CH_2O_3, always splits up into water and carbon dioxide, which escapes as gas. The corresponding sulphur compound, CH_2S_3, is, however, obtained as an oily liquid when a metallic thio-carbonate is decomposed by an acid (i. 219).

With the alkali-metals carbonic acid forms acid and normal or neutral salts, according as one or both of the hydrogen-atoms are replaced ; *e.g.* :

Acid sodium carbonate, $CHNaO_3$, or $CO<\begin{smallmatrix}OH\\ ONa\end{smallmatrix}$
Normal sodium carbonate, CNa_2O_3, or $CO(ONa)_2$.

With dyad-metals, carbonic acid forms only normal salts, $CM''O_3$, and basic salts ; the so-called acid carbonates of barium, calcium, &c., are known only in solution, and are, in fact, merely solutions of neutral carbonates in aqueous carbonic acid, which give off carbon dioxide on boiling. The basic carbonates of dyad metals may be viewed as compounds of normal carbonates with metallic oxides or hydrates; for example, slaked lime, produced by exposing quicklime to moist air, has the composition of a dicalcic carbonate, $CaO.CaCO_3.aq.$; and native green copper carbonate, or malachite, consists of $CuO.CuCO_3 + H_2O$. These basic carbonates may, however, be viewed in another way, namely, as derived from a tetratomic carbonic acid, or ortho-carbonic acid, CH_4O_4 or $C(OH)_4$, analogous to methane and carbon tetrachloride; thus, dicalcic carbonate $= CCa_2O_4 + H_2O$; malachite $= CCu_2O_4 + H_2O$.

With metals of higher atomicity, carbonic acid does not form definite salts.

CARBONIC ETHERS.—The only carbonic ethers known are those in which the two hydrogen-atoms of carbonic acid are replaced either by two equivalents of a monad alcohol-radicle, or by one equivalent of a monad alcohol-radicle and one equivalent of metal.

Ethyl carbonate $(C_2H_5)_2CO_3$, is formed by the action of ethyl iodide on silver carbonate:

$$Ag_2CO_3 + 2C_2H_5I = 2AgI + (C_2H_5)C_2O_3;$$

also by the action of potassium or sodium on ethyl oxalate, $(C_2H_5)_2C_2O_4$; this reaction is not quite understood, but it amounts to the removal of carbon monoxide, or carbonyl, CO, from the oxalic ether. Fragments of potassium or sodium are dropped into oxalic ether as long as gas is disengaged: the brown pasty product is then mixed with water and distilled. The carbonic ether is found floating upon the surface of the water of the receiver as a colourless, limpid liquid of aromatic odour and burning taste. It boils at 125° degrees, and is decomposed by an alcoholic solution of potash into potassium carbonate and alcohol. By chlorine in diffused daylight it is converted into dichlorethyl carbonate, $(C_2H_3Cl_2)_2CO_3$, and in sunshine into pentachlorethyl carbonate, $(C_2Cl_5)_2CO_3$.

Ethyl-potassium carbonate $(C_2H_5)KCO_3$, is produced by passing carbonic acid gas into a cooled solution of potassium hydroxide in absolute alcohol:

$$C_2H_6O + KHO + CO_2 = H_2O + (C_2H_5)KCO_3.$$

It is a white nacreous salt, decomposed by water into potassium carbonate, and alcohol.

Ethyl-methyl carbonate, $(C_2H_5)(CH_3)CO_3$, is obtained by distilling a mixture of ethyl-potassium sulphate and methyl-potassium carbonate:

$$(C_2H_5)K.SO_4 + (CH_3)K.CO_3 = K_2SO_4 + (C_2H_5)(CH_3).CO_3.$$

Methyl-barium carbonate, $(CH_3)_2Ba(CO_3)_2$, is obtained as a white precipitate by passing carbonic acid gas into a solution of baryta in methyl alcohol.

Carbonates of *butyl*, *amyl*, and *allyl*, analogous in composition to ethyl carbonate, have also been obtained. *Phenyl-hydrogen carbonate*, or *acid phenyl carbonate*, $(C_6H_5)HCO_3$, is identical with salicylic acid, which will be described further on.

Ethyl orthocarbonate $C(OC_2H_5)_4$, is produced by heating a mixture of chloropicrin (trichloro-nitromethane) with absolute alcohol and sodium:

$$\underset{\text{Chloropicrin.}}{C(NO_2)Cl_3} + \underset{\substack{\text{Sodium}\\\text{ethylate.}}}{4NaOC_2H_5} = \underset{\substack{\text{Sodium}\\\text{chloride.}}}{3NaCl} + \underset{\substack{\text{Sodium}\\\text{nitrite.}}}{NaNO_2} + \underset{\substack{\text{Ethyl-ortho-}\\\text{carbonate.}}}{C(OC_2H_5)_4}$$

It is a colourless oil, boiling at 158°–159°.

Thiocarbonic or Sulphocarbonic Ethers.—These are bodies having the composition of carbonic ethers in which the oxygen is replaced, wholly or partly, by sulphur. The following table exhibits their names and formulæ, the ethyl and ethene compounds being taken as examples :

Ethyl-monothiocarbonic acid,	$(C_2H_5)H.CO_2S$.
Diethylic monothiocarbonate,	$(C_2H_5)_2.CO_2S$.
Ethyl-dithiocarbonic or Xanthic acid,	$(C_2H_5)H.COS_2$.
Diethylic dithiocarbonate,	$(C_2H_5)_2.COS_2$.
Ethyl-trithiocarbonic acid,	$(C_2H_5)H.CS_3$.
Diethylic trithiocarbonate,	$(C_2H_5)_2.CS_3$.
Ethene dithiocarbonate,	$(C_2H_4).COS_2$.
Ethene trithiocarbonate,	$(C_2H_4)CS_3$.

The metallic salts of the acid thiocarbonic ethers are produced in the same manner as those of the carbonic ethers : thus carbon dioxide unites with potassium sulphethylate (mercaptide), to form potassium ethylmonothiocarbonate, just as it unites with potassium ethylate to form the ethylcarbonate ; and, in like manner, carbon bisulphide acts on potassium ethylate or alcoholic potash, so as to form potassium ethyldithiocarbonate ; and on potassium mercaptide, or an alcoholic solution of the sulphhydrate, so as to form the ethyltrithiocarbonate, thus:

$$CO_2 + (C_2H_5)KO = (C_2H_5)KCO_3 \quad \text{Ethylcarbonate.}$$
$$CO_2 + (C_2H_5)KS = (C_2H_5)KCO_2S \quad \text{Ethylmonothiocarbonate.}$$
$$CS_2 + (C_2H_5)KO = (C_2H_5)KCOS_2 \quad \text{Ethyldithiocarbonate.}$$
$$CS_2 + (C_2H_5)KS = (C_2H_5)KCS_3 \quad \text{Ethyltrithiocarbonate.}$$

The neutral thiocarbonic ethers (containing monatomic alcohol-radicles) are produced by the action of the chlorides, bromides, &c., of alcohol-radicles on the metallic salts of the corresponding acid ethers ; *e.g.*:

$$(C_2H_5)KCS_3 + C_2H_5Cl = KCl + (C_2H_5)_2CS_3.$$

The thiocarbonic ethers of diatomic alcohol-radicles are formed by the action of diatomic alcoholic bromides, iodides, &c., on sodium thiocarbonate ; *e.g.*:

$$C_2H_4Br_2 + Na_2CS_3 = 2NaBr + (C_2H_4)CS_3.$$

The neutral thiocarbonic ethers are oily liquids; so likewise are the acid ethers, such at least as are known in the free state, or as hydrogen salts; their metallic salts are mostly crystalline. The best known of these compounds are the ethyl-dithiocarbonates or xanthates.

To prepare xanthic acid, alcohol of 0·800 specific gravity is saturated, whilst boiling, with potash, and into this solution carbon bisulphide is dropped till it ceases to be dissolved, or until the liquid loses its alkalinity. On cooling the whole to −18°, the potassium-salt separates in the form of brilliant, slender, colourless prisms, which must be quickly pressed between folds of bibulous paper, and dried in a vacuum. It is freely soluble in water and alcohol, but insoluble in ether, and is gradually destroyed by exposure to air, by oxidation of part of the sulphur. Xanthic acid may be prepared by decomposing this salt with dilute sulphuric or hydrochloric acid. It is a colourless, oily liquid, heavier than water, of powerful and peculiar odour, and very combustible: it reddens litmus-paper, and ultimately bleaches it. Exposed to gentle heat (about 24°), it is decomposed into alcohol and carbon bisulphide. Exposed to the air, or kept beneath the surface of water open to the air, it becomes covered with a whitish crust, and is gradually destroyed. The xanthates of the alkali-metals and of barium are colourless and crystallisable; the calcium salt dries up to a gummy mass; the xanthates of zinc, lead, and mercury are white, and but slightly soluble; that of copper is a flocculent, insoluble substance, of beautiful yellow colour.

Ethylic dithiocarbonate or *Xanthic ether*, $(C_2H_5)_2.COS_2$, obtained by the action of ethyl chloride on potassium xanthate, is a pale-yellow oil, boiling at 200°, insoluble in water, soluble in all proportions of alcohol or ether. Ammonia-gas passed into its alcoholic solution forms mercaptan and a crystalline substance, $CO<^{SC_2H_5}_{NH_2}$, called xanthamide:

$$CO<^{SC_2H_5}_{SC_2H_5} + NH_3 = C_2H_5SH + CO<^{SC_2H_5}_{NH_2}.$$

Amyl dithiocarbonate, $CO(SC_5H_{11})_2$, treated in like manner, yields amylxanthamide, $CO<^{SC_5H_{11}}_{NH_2}$.

Chlorocarbonic Ethers, CO_2ClR or $CO<^{Cl}_{OR}$, [R denoting a monatomic alcohol-radicle.]—These compounds, derived from carbonic ethers, $CO(OR)_2$, by substitution of Cl for one of the groups OR, are formed by the action of carbonyl chloride (phosgene) on the alcohols; *e.g.:*

$$CO<^{Cl}_{Cl} + HOCH_3 = HCl + CO<^{Cl}_{OCH_3}.$$

Methyl chlorocarbonate, $CO_2Cl(CH_3)$, is a colourless mobile oil, heavier and more volatile than water, having a pungent odour, and burning with a greenish flame. Gaseous ammonia converts it into methyl carbamate (urethane):

$$CO<^{Cl}_{OCH_3} + NH_3 = HCl + CO<^{NH_2}_{OCH_3}.$$

Ethyl chlorocarbonate, $CO_2Cl(OC_2H_5)$, is also a colourless, very mobile liquid, the vapour of which is very irritating to the eyes. Specific gravity 1·139 at 13°. Boiling point, 94°. It is very inflammable, burns with a green flame, is decomposed by hot water, and quickly converted by ammonia into ethyl carbamate.

DIATOMIC AND BIBASIC ACIDS.

These acids contain the group, CO_2H, twice, and must therefore contain four atoms of oxygen. They may all be included in the general formula, $R''(CO_2H)_2$,—R denoting a diatomic hydrocarbon-radicle,—or they may be regarded as compounds of oxygenated radicles with two equivalents of hydroxyl, *e.g.*, succinic acid $= (C_4H_4O_2)''(OH)_2$.

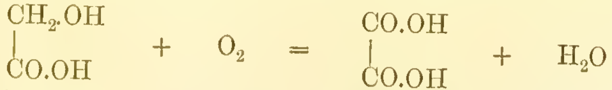
1.—Oxalic or Succinic Series, $C_nH_{2n-2}O_4$, or $C_nH_{2n}<\begin{matrix}CO.OH\\CO.OH\end{matrix}$.

The known acids of this series are:

Oxalic acid, . . .	$C_2H_2O_4$	Pimelic acid, . .	$C_7H_{12}O_4$
Malonic acid, . .	$C_3H_4O_4$	Suberic acid, . .	$C_8H_{14}O_4$
Succinic acid, . .	$C_4H_6O_4$	Anchoic acid, . .	$C_9H_{16}O_4$
Pyrotartaric acid, .	$C_5H_8O_4$	Sebic acid, . . .	$C_{10}H_{18}O_4$
Adipic acid, . . .	$C_6H_{10}O_4$	Roccellic acid, . .	$C_{17}H_{32}O_4$

They are produced:—1. By oxidation of the corresponding glycols, $R''(CH_2OH)_2$, the change consisting in the substitution of O_2 for H_4 (p. 267). In this manner oxalic acid, $C_2H_2O_4$, is formed from ethene alcohol, $C_2H_6O_2$, and malonic acid, $C_3H_4O_4$, from β-propene alcohol, $C_3H_8O_2$; but all the known glycols of higher order split up under the influence of oxidising agents, and do not yield bibasic acids containing the same number of carbon-atoms as themselves.

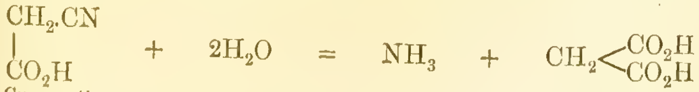
2. By oxidation of the oxyfatty acids, $C_nH_{2n}O_3$, in which the hydroxyl-group is directly attached to the group CH_2; *e.g.*:



$$\begin{matrix}CH_2.OH\\ |\\ CO.OH\end{matrix} + O_2 = \begin{matrix}CO.OH\\ |\\ CO.OH\end{matrix} + H_2O$$

Glycollic acid. Oxalic acid.

3. By boiling the cyano-derivatives of the fatty acids with alkalis or acids:



$$\begin{matrix}CH_2.CN\\ |\\ CO_2H\end{matrix} + 2H_2O = NH_3 + CH_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

Cyanacetic acid. Malonic acid.

4. By boiling the cyanides of diatomic alcohol-radicles with alcoholic potash; *e.g.*:

$$(C_3H_6)(CN)_2 + 2KOH + 2H_2O = 2NH_3 + (C_3H_6)(CO_2K)_2$$

Propene cyanide. Potassium pyrotartrate.

This reaction is analogous to that by which the fatty acids are formed from the cyanides of the monatomic alcohol-radicles, C_nH_{2n+1} (p. 270).

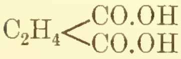
5. By the addition of hydrogen to other acids containing a smaller proportion of that element; in this manner succinic acid, $C_4H_6O_4$, is formed from fumaric acid, $C_4H_4O_4$.

6. By the action of heat on acids of more complicated structure; *e.g.*:

$$\underset{\text{Tartaric acid.}}{2C_4H_6O_6} = 3CO_2 + 2H_2O + \underset{\text{Pyrotartaric acid.}}{C_5H_8O_4}$$

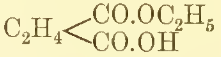
7. Many of these acids are produced by the action of powerful oxidisers on a variety of organic bodies: thus, succinic, adipic, pimelic, suberic, and anchoic acids are produced by treating various fatty and resinous bodies with nitric acid.

The acids of this series are solid, crystallisable, non-volatile bodies, for the most part easily soluble in water, and having a strong acid reaction. Being bibasic, they form acid and neutral salts, and acid and neutral ether; thus:



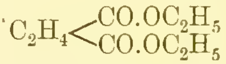
$$C_2H_4<{CO.OH \atop CO.OH}$$

Succinic acid.



$$C_2H_4<{CO.OC_2H_5 \atop CO.OH}$$

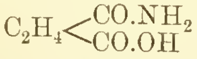
Ethyl-succinic acid.



$$C_2H_4<{CO.OC_2H_5 \atop CO.OC_2H_5}$$

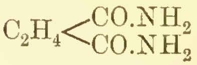
Diethylic succinate.

In like manner, each acid can form an acid amide or amic acid, and a neutral amide or diamide by substitution of amidogen, NH_2, for one or both of the hydroxyl groups, also a neutral imide by substitution of the bivalent-radicle imidogen, NH, for both these groups together; thus:



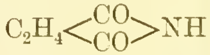
$$C_2H_4<{CO.NH_2 \atop CO.OH}$$

Succinamic acid.



$$C_2H_4<{CO.NH_2 \atop CO.NH_2}$$

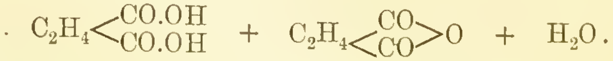
Succinamide.



$$C_2H_4<{CO \atop CO}>NH$$

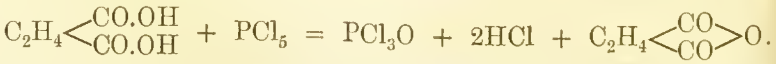
Succinimide.

These bibasic acids, when heated, give off their water, and yield anhydrides which, when boiled with water, are reconverted into the acids:



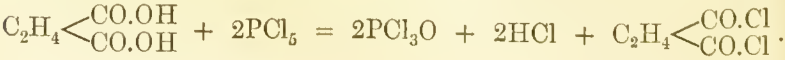
$$C_2H_4<{CO.OH \atop CO.OH} + C_2H_4<{CO \atop CO}>O + H_2O.$$

The anhydrides are also produced by treating the acids with phosphorous pentachloride:

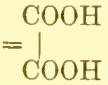


$$C_2H_4<{CO.OH \atop CO.OH} + PCl_5 = PCl_3O + 2HCl + C_2H_4<{CO \atop CO}>O.$$

With excess of phosphorus pentachloride, acid chlorides or chloranhydrides are produced; thus:



$$C_2H_4<{CO.OH \atop CO.OH} + 2PCl_5 = 2PCl_3O + 2HCl + C_2H_4<{CO.Cl \atop CO.Cl}.$$

Oxalic Acid, $C_2H_2O_4 =$  $\begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array}$ $= (C_2O_2)''(OH)_2$.—This important acid exists ready formed in many plants as a potassium or calcium-salt, and is produced by the oxidation of a great variety of organic compounds. In some cases the reaction consists in a definite substitution of oxygen for hydrogen; thus oxalic acid is formed from ethene alcohol, $C_2H_6O_2$, by substitution of O_2 for H_4, and from ethyl alcohol, C_2H_6O, by the same substitution and further addition of one atom of oxygen. But in most cases the reaction is more complex, consisting in a complete breaking up of the molecule. In this manner oxalic acid is produced in great abundance from more highly carbonised organic substances, such as sugar, starch, cellulose, &c., by the action of nitric acid, or by fusion with caustic alkalis.

Oxalic acid is also produced: *α*. As a sodium or potassium salt by direct combination of the alkali-metal with carbon dioxide:

$$2CO_2 + Na_2 = C_2O_4Na_2 .$$

The sodium salt is obtained by passing carbon dioxide over a heated mixture of sodium and sand; the potassium-salt by heating potassium-amalgam in the gas.*

β. As an ammonium salt, together with other products, in the decomposition of cyanogen by water:

$$C_2N_2 + 4H_2O = C_2(NH_4)_2O_4 .$$

γ As a potassium salt by heating potassium formate with excess of potash:

$$2CHKO_2 = C_2K_2O_4 + H_2 .$$

Preparation.—1. By the oxidation of sugar with nitric acid:

$$C_{12}H_{22}O_{11} + O_{18} = 6C_2H_2O_4 + 5H_2O .$$

One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1·42, diluted with twice its weight of water; copious red fumes are then disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, redissolved in a small quantity of hot water, and the solution is set aside to cool.

2. By heating sawdust with caustic alkali. Many years ago, Gay-Lussac observed that wood and several other organic substances were converted into oxalic acid by fusion with caustic potash. Upon this observation, Messrs. Roberts, Dale, & Co. have founded a method for the preparation of oxalic acid, which furnishes this acid at a much cheaper rate than any other process. A mixed solution of the hydrates of sodium and potassium,

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* Kolbe and Drechsel, Chem. Soc. Journal [2], vi. 121.

in the proportion of two molecules of the former to one of the latter, is evaporated to about 1·35 sp. gr., and then mixed with sawdust, so as to form a thick paste, which is placed in thin layers on iron plates. The mixture is now gradually heated, care being taken to keep it constantly stirred. The action of heat expels a quantity of water, and the mass intumesces strongly, with disengagement of much inflammable gas, consisting of hydrogen and carburetted hydrogen. The mixture is now kept for some hours at a temperature of 400° F. (204° C.), care being taken to avoid charring, which would cause a loss of oxalic acid. The product thus obtained is a grey powder; it is now treated with water at about 60° F. (15·5° C.), which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off, evaporated to dryness, and heated in furnaces to recover the alkalis, which are caustified and used for a new operation. The sodium oxalate is washed and decomposed by boiling with slaked lime, and the resulting calcium oxalate is decomposed by means of sulphuric acid. The liquid decanted from the calcium sulphate is evaporated to crystallisation in leaden vessels, and the crystals are purified by re-crystallisation.

Oxalic acid separates from a hot solution in colourless, transparent crystals derived from an oblique rhombic prism, and consisting of $C_2H_2O_4.2H_2O$. The two molecules of crystallisation-water may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, consisting of anhydrous oxalic acid, $C_2H_2O_4$, which may be sublimed in great measure without decomposition. The crystallised acid, on the contrary, is decomposed by a high temperature into formic acid, carbon monoxide, and carbon dioxide, without leaving any solid residue:

$$2C_2H_2O_4 = CH_2O_2 + CO + 2CO_2 + H_2O.$$

The crystals of oxalic acid dissolve in 8 parts of water at 15·5°, and in their own weight, or less, of hot water: they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbon monoxide and carbon dioxide: it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture from sugar. The dioxides of lead and manganese effect the same change, becoming reduced to monoxides, which form salts with the unaltered acid.

Oxalates.—Oxalic acid, like other bibasic acids, forms with monatomic metals, neutral or normal salts containing $C_2M_2O_4$, and acid salts, C_2HMO_4. With potassium and ammonium it likewise forms hyper-acid salts, *e.g.*, $C_2HKO_4.C_2H_2O_4$, or $C_4H_3KO_8$. With most diatomic metals it forms only neutral salts, $C_2M''O_4$; with barium and strontium, however, it forms acid salts analogous to the hyper-acid oxalates of the alkali-metals. It also forms numerous well-crystallised double salts. It is one of the strongest acids, decomposing dry sodium chloride when heated, with evolution of hydrochloric acid, and converting sodium chloride or nitrate in aqueous solution into acid oxalate.

The oxalates of the alkali-metals are soluble in water; the rest are for the most part insoluble in water, but soluble in dilute acids.

All oxalates are decomposed by heat. The oxalates of the alkali-metals, and also of the alkaline earth-metals, if not too strongly heated, give off carbon monoxide and leave carbonates, while the oxalates of those metals whose carbonates are decomposed by heat (zinc and magnesium, for example) give off carbon monoxide and carbon dioxide, and leave metallic oxides. The oxalates of the more easily reducible metals (silver and copper, &c.), give off carbon dioxide and leave the metal; the lead-salt leaves suboxide of lead, and gives off 3 volumes of carbon dioxide to 1 volume of carbon monoxide:

$$2C_2PbO_4 = Pb_2O + 3CO_2 + CO .$$

Oxalates heated with *sulphuric acid* give off carbon monoxide and dioxide, and leave a residue of sulphate. In this case, as well as in the decomposition by heat alone, no separation of carbon takes place, and consequently the residue does not blacken: this character distinguishes the oxalates from the salts of all other carbon acids.

Oxalic acid and the soluble oxalates give with *calcium chloride* a precipitate of calcium oxalate, insoluble in water and in acetic acid, but soluble in hydrochloric and nitric acid. This reaction affords a very delicate test for the presence of oxalic acid: the insolubility of the precipitated oxalate in acetic acid distinguishes it at once from the phosphate.

POTASSIUM OXALATES.—The *neutral salt*, $C_2K_2O_4.2$ aq., prepared by neutralising oxalic acid with potassium carbonate, crystallises in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water.—The *acid oxalate* or *binoxalate*, $C_2HKO_4.2$ aq., sometimes called *Salt of Sorrel*, from its occurrence in that plant, is found also in other species of *Rumex*, in *Oxalis acetosella*, and in garden rhubarb, associated with malic acid. It is easily prepared by dividing a solution of oxalic acid in hot water into two equal portions, neutralising one with potassium carbonate, and adding the other: the salt crystallises, on cooling, in colourless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution. A solution of this salt is often used for removing ink from paper. The *hyper-acid oxalate* or *quadroxalate*, $C_2HKO_4.C_2H_2O_4.2$ aq., is prepared by saturating 1 part of oxalic acid with potassium carbonate, and adding 3 parts of oxalic acid. The crystals are triclinic, and dissolve in 20 parts of water at 20°.

Sodium oxalate, $C_2Na_2O_4$, is slightly soluble and difficult to crystallise. The *acid salt*, C_2HNaO_4, forms crystals which redden litmus.

AMMONIUM OXALATES.—The *neutral salt*, $C_2(NH_4)_2O_4 + 2\,aq.$, is prepared by neutralising a hot solution of oxalic acid with ammonium carbonate. It crystallises in long, colourless, rhombic prisms, which effloresce in dry air. They are not very soluble in cold water, but dissolve freely with the aid of heat.

The dry salt, when heated in a retort, gives off water, and yields a sublimate of oxamide:*

$$\underset{\text{Ammonium oxalate.}}{(C_2O_2)(ONH_4)_2} = 2H_2O + \underset{\text{Oxamide.}}{(C_2O_2)(NH_2)_2}$$

When distilled with phosphoric oxide, it gives up four molecules of water, and yields a considerable quantity of cyanogen, $C_2(NH_4)_2O_4 - 4H_2O = 2CN$. Other products are, however, formed at the same time.

Acid ammonium oxalate, or *binoxalate*, $C_2H(NH_4)O_4 + aq.$, is still less soluble than the neutral salt. When heated in an oil-bath to 232°, it loses one molecule of water, and yields oxamic acid, $C_2H_3NO_3$, or $(C_2O_2)(OH)(NH_2)$, and other products.

CALCIUM OXALATE, $C_2CaO_4 + 4\,aq.$—This salt occurs in the juice of most plants, and separates out towards the end of the growing season in microscopic octohedral crystals; it is also a frequent constituent of urinary deposits and calculi. It is formed whenever oxalic acid or an oxalate is added to a soluble calcium-salt; it falls as a white powder, which acquires density by boiling, and is but little soluble in dilute hydrochloric, and quite insoluble in acetic acid. Nitric acid dissolves it easily. When dried at 100°, it retains a molecule of water, which may be driven off by a rather higher temperature. Exposed to a red heat in a close vessel, it is converted into calcium carbonate, with escape of carbon monoxide.

The oxalates of *barium, zinc, manganese, copper, nickel, cobalt*, and *ferrous oxalate*, are nearly insoluble in water: *magnesium oxalate* is sparingly soluble: *ferric oxalate* is freely soluble.—*Potassio-chromic oxalate*, $K_3Cr(C_2O_4)_3 + 3\,aq.$, prepared by dissolving in hot water 1 part of potassium bichromate, 2 parts of potassium binoxalate, and 2 parts of crystallised oxalic acid, is one of the most beautiful salts known. The crystals appear black by reflected light, from the intensity of their colour, which is pure deep blue: they are very soluble. A corresponding *potassio-ferric oxalate* has been formed: it crystallises freely, and has a fine green colour.

ETHYL OXALATES.—The *neutral oxalate*, or *Oxalic ether*, $C_2O_4(C_2H_5)_2 = C_2O_2(OC_2H_5)_2$, is most easily obtained by distilling together 4 parts of potassium binoxalate, 5 parts of oil of vitriol, and 4 parts of strong alcohol. The distillation may be pushed nearly to dryness, and the receiver kept warm, to dissipate any ethyl oxide that may be formed. The product is mixed with water, by which the oxalic ether is separated from the undecomposed spirit: it is repeatedly washed to remove adhering acid, and re-distilled in a small retort, the first portion being collected apart and rejected. Another very simple process consists in digesting equal parts of alcohol and dehydrated oxalic acid in a flask furnished with a long glass tube in which the volatilised spirit may condense. After six or eight hours' digestion, the mixture generally contains only traces of unetherified oxalic acid.

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* See the Chapter on Amides.

Pure oxalic ether is a colourless, oily liquid, of pleasant aromatic odour, and 1·09 specific gravity. It boils at 183·8°, is but little soluble in water, and is readily decomposed by caustic alkalis into a metallic oxalate and alcohol. With solution of ammonia in excess, it yields oxamide and alcohol; thus:

$$(C_2O_2)(OC_2H_5)_2 + 2NH_3 = 2(HOC_2H_5) + (C_2O_2)(NH_2)_2 .$$

This is the best process for preparing oxamide.

When dry gaseous ammonia is conducted into a vessel containing oxalic ether, the gas is rapidly absorbed, and a white solid substance produced, which is soluble in hot alcohol, and separates on cooling in colourless, transparent, scaly crystals. They dissolve in water, and are both fusible and volatile. This substance is oxamethane, the ethylic ether of oxamic acid;*

$$(C_2O_2)(OC_2H_5)_2 + NH_3 = HOC_2H_5 + C_2O_2(NH_2)(OC_2H_5) .$$

The same substance is formed when ammonia in small quantity is added to a solution of oxalic ether in alcohol.

When oxalic ether is treated with excess of dry chlorine in sunshine, a white, colourless, crystalline, fusible body is produced, insoluble in water, and instantly decomposed by alcohol. It consists of perchlorethylic oxalate, $C_8Cl_{10}O_4$, or $(C_2Cl_5)_2C_2O_4$, or oxalic ether in which the whole of the hydrogen is replaced by chlorine.

Ethyl oxalate is converted by potassium or sodium into ethyl carbonate, with evolution of carbon monoxide: $C_2(C_2H_5)_2O_4 = C(C_2H_5)_2O_3 + CO$; but the reaction is complicated by the formation of several other products.

When ethyl oxalate is agitated with sodium amalgam in a vessel externally cooled, a product is obtained which is separated by ether into a soluble and an insoluble portion, the latter consisting of fermentable sugar, together with sodium oxalate, and at least one other sodium-salt, while the ethereal solution yields, by spontaneous evaporation, crystals having the composition $C_{11}H_{18}O_8$, and consisting of the ethylic ether of a tribasic acid, $C_5H_6O_8$, called deoxalic acid, because it is produced by deoxidation of oxalic acid: $5C_2H_2O_4 + 5H_2 = 2C_5H_6O_8 + 4H_2O$; and racemocarbonic acid, because it contains the elements of racemic acid, $C_4H_6O_6$, and carbon dioxide, CO_2, and is resolved into those two compounds when its aqueous solution is heated in a sealed tube with a small quantity of sulphuric acid. The decomposition of ethylic oxalate by sodium amalgam has not been completely investigated, but the formation of deoxalic acid and glucose may be represented by the equation:

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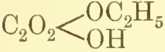
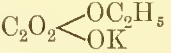
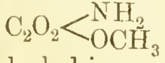
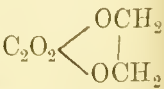
* See the Chapter on Amides.

$$8C_2H_2O_4 + 14H_2 = 2C_5H_6O_8 + C_6H_{12}O_6 + 10H_2O .$$

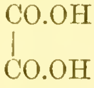
Ethyl oxalate, treated with zinc-ethyl, and afterwards with water, yields the ethylic ether of diethoxalic acid, $C_2H_2(C_2H_5)_2O_3$, and similar products with zinc-methyl and zinc-amyl (p. 305).

Acid ethyl oxalate, or *Ethyloxalic acid*, $C_2H(C_2H_5)O_4$, or  $C_2O_2{<}\begin{smallmatrix}OC_2H_5\\OH\end{smallmatrix}$, is obtained as a potassium-salt by adding to a solution of neutral ethyl oxalate in absolute alcohol, a quantity of alcoholic potash less than sufficient to convert the whole into potassium oxalate and alcohol; on dissolving this salt in hydrated alcohol, carefully saturating with sulphuric acid, and neutralising with carbonate of lead or barium, the ethyloxalate of lead or barium is obtained.—The acid itself is prepared by decomposing either of these salts with sulphuric acid; but it is very unstable, and is decomposed by concentration into alcohol and oxalic acid. The *potassium salt*,  $C_2O_2{<}\begin{smallmatrix}OC_2H_5\\OK\end{smallmatrix}$, forms crystalline scales, which begin to decompose towards 100°.

METHYL OXALATE, $C_2(CH_3)_2O_4$, or $C_2O_2(OCH_3)_2$, is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spirituous liquid collects in the receiver, which, when exposed to the air, quickly evaporates, leaving the methyl oxalate in the form of rhombic, transparent, crystalline plates, which may be purified by pressure between folds of bibulous paper, and redistilled from a little oxide of lead. The product is colourless, and has the odour of ethyl oxalate; it melts at 51°, and boils at 161°; dissolves freely in alcohol and wood-spirit, also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxamide and methyl alcohol. With dry ammoniacal gas it yields methyl oxamate, or oxamethylane,  $C_2O_2{<}\begin{smallmatrix}NH_2\\OCH_3\end{smallmatrix}$, a white, solid substance, which crystallises from alcohol in pearly cubes.

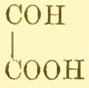
ETHENE OXALATE, $C_2O_4(C_2H_4)$, or $(C_2O_2)(C_2H_4O_2) =$  $C_2O_2{<}\begin{smallmatrix}OCH_2\\|\\OCH_2\end{smallmatrix}$, appears to be formed by the action of ethene bromide on silver oxalate.

Closely related to oxalic acid are glyoxylic acid, $C_2H_2O_3$, and glyoxal, $C_2H_2O_2$, which may be regarded as aldehydic derivatives of oxalic acid or of glycol:



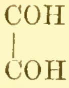
$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array}$$

Oxalic acid.



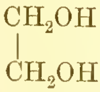
$$\begin{array}{l}COH\\ |\\ COOH\end{array}$$

Glyoxylic acid.



$$\begin{array}{l}COH\\ |\\ COH\end{array}$$

Glyoxal.

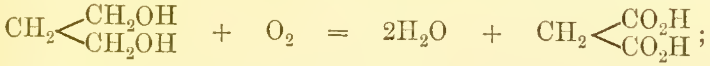


$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

Glycol.

Both are formed as intermediate products in the oxidation of glyco and are converted by further oxidation into oxalic acid (see ALDEHYDES, p. 256).

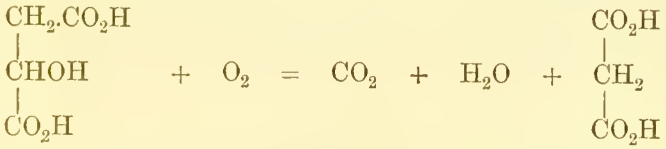
Malonic Acid, $C_3H_4O_4 = CH_2<^{CO_2H}_{CO_2H}$.—This acid is formed: 1. By gradual oxidation of β-propene glycol:



$$CH_2<^{CH_2OH}_{CH_2OH} + O_2 = 2H_2O + CH_2<^{CO_2H}_{CO_2H};$$

also by oxidation of propene and allylene.

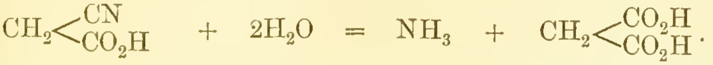
2. By oxidising malic acid with chromic acid mixture:



$$\begin{array}{l}CH_2.CO_2H\\ |\\ CHOH\\ |\\ CO_2H\end{array} + O_2 = CO_2 + H_2O + \begin{array}{l}CO_2H\\ |\\ CH_2\\ |\\ CO_2H\end{array}$$

3. By decomposition of barbituric acid (Malonyl-urea: see AMIDES).

4. Synthetically by the action of alkalis on cyanacetic acid, better, on its ethylic ether:



$$CH_2<^{CN}_{CO_2H} + 2H_2O = NH_3 + CH_2<^{CO_2H}_{CO_2H}.$$

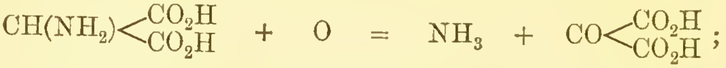
Ethylic monochloracetate is heated with solution of potassiun cyanide, and the product is boiled with potash as long as it continues to give off ammonia. The alkaline solution is then acidulated with sulphuric acid, and the free malonic acid extracted by ether.

Malonic acid crystallises in large rhombohedral plates; dissolves easily in water, alcohol, and ether; melts at 132°; and decomposes at a higher temperature into acetic acid and carbon dioxide. Its *barium salt*, $C_3H_2BaO_4 + H_2O$, forms silky needles. The *calcium salt*, $4C_3H_2CaO_4 + 7H_2O$, is very slightly soluble in cold water.

Nitrosomalonic Acid, $CH(NO)<^{CO_2H}_{CO_2H}$, formed by heating violuric acid (*q.v.*) with alkalis, crystallises in shining needles, easily soluble in water. When heated it melts, and then explodes.

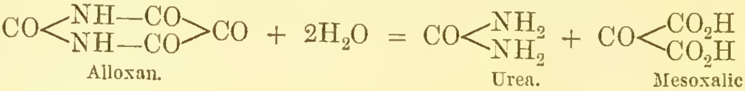
Amidomalonic Acid, $CH(NH_2)<\substack{CO_2H\\CO_2H}$, produced by the action of sodium-amalgam on the nitroso-acid, forms shining prisms, which, when heated, are resolved into carbon dioxide and amidacetic acid, $CH_2(NH_2)—CO_2H$.

Mesoxalic Acid, $C_3H_2O_5 = CO<\substack{CO_2H\\CO_2H}$.—This ketonic acid, derived from malonic acid by substitution of O for H_2 in the group CH_2, is produced by oxidising amidomalonic acid by means of iodine in an aqueous solution containing potassium iodide :



$$CH(NH_2)<\substack{CO_2H\\CO_2H} \quad + \quad O \quad = \quad NH_3 \quad + \quad CO<\substack{CO_2H\\CO_2H} ;$$

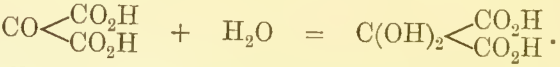
also by boiling alloxan (mesoxalyl-urea *q.v.*) with alkalis :



$$CO<\substack{NH—CO\\NH—CO}>CO \ + \ 2H_2O \ = \ CO<\substack{NH_2\\NH_2} \ + \ CO<\substack{CO_2H\\CO_2H}$$

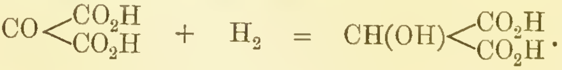
Alloxan. Urea. Mesoxalic acid.

Mesoxalic acid crystallises in deliquescent prisms, containing 1 mol. water, easily soluble in alcohol and ether. It melts at 115° without giving off its water of crystallation, and decomposes at a higher temperature. The water appears therefore to be very intimately combined, probably in the form represented on the right-hand side of the following equation :



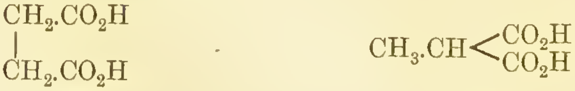
$$CO<\substack{CO_2H\\CO_2H} \quad + \quad H_2O \quad = \quad C(OH)_2<\substack{CO_2H\\CO_2H} .$$

The metallic mesoxalates and the ethylic ether also contain 1 mol. water very intimately combined ; the ether probably has the constitution $C(OH)_2(CO_2C_2H_5)_2$. The *barium salt*, $C_3BaO_5 + 1\frac{1}{2}H_2O$, is nearly insoluble in water. The *silver salt*, $C_3Ag_2O_5 + H_2O$, is an amorphous powder, which blackens on exposure to light, and is decomposed by boiling with water into mesoxalic acid, metallic silver, silver oxalate, and carbon dioxide. By the action of sodium-amalgam mesoxalic acid is converted into tartronic acid :



$$CO<\substack{CO_2H\\CO_2H} \quad + \quad H_2 \quad = \quad CH(OH)<\substack{CO_2H\\CO_2H} .$$

Succinic Acids, $C_4H_6O_4 = C_2H_4<\substack{CO_2H\\CO_2H}$.—Of these acids there are two modifications, viz. :

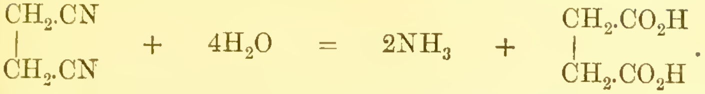


$$\begin{matrix}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{matrix} \qquad\qquad CH_3.CH<\substack{CO_2H\\CO_2H}$$

Succinic. Isosuccinic.

1. **Ordinary Succinic, β-Succinic,** or **Ethene-dicarbonic Acid,** is produced :

1. By heating ethene cyanide with alcoholic potash:



$$\begin{array}{l}CH_2.CN\\ \vert\\ CH_2.CN\end{array} + 4H_2O = 2NH_3 + \begin{array}{l}CH_2.CO_2H\\ \vert\\ CH_2.CO_2H\end{array}.$$

2. By converting β-iodopropionic acid into the corresponding cyanogen derivative, and decomposing the latter with alkalis or acids:

$$\underset{\beta\text{-Cyanopropionic acid.}}{CH_2.CN—CH_2—CO_2H} + 2H_2O = NH_3 + \underset{\beta\text{-Succinic acid.}}{CH_2.CO_2H—CH_2—CO_2H}.$$

3. By the action of nascent hydrogen (evolved by sodium-amalgam) on maleic acid, or its isomeride, fumaric acid: $C_4H_4O_4 + H_2 = C_4H_6O_4$.

4. By the action of hydriodic acid (or water and phosphorus iodide) on malic acid, $C_4H_6O_5$, or tartaric acid, $C_4H_6O_6$, the reaction consisting in the abstraction of 1 or 2 atoms of oxygen, with formation of water and separation of iodine.

5. By the fermentation of malic or fumaric acid and of many other organic substances, especially under the influence of putrefying casein; in small quantity also during the alcoholic fermentation of sugar (p. 123, foot-note).

6. By the oxidation of many organic substances, especially of the fatty acids, $C_nH_{2n}O_2$, and their glycerides, under the influence of nitric acid. Its formation from butyric acid is represented by the equation $C_4H_8O_2 + O_3 = H_2O + C_4H_6O_4$.

Succinic acid occurs ready formed in amber and in certain lignites, and occasionally in the animal organism. By heating amber in iron retorts, it may be obtained in coloured crystals, which may be purified by treatment with nitric acid and recrystallisation from boiling water. It is, however, more advantageously prepared by the fermentation of malic acid, the crude calcium malate obtained by neutralising the juice of mountain-ash berries with chalk or slaked lime being used for the purpose. The salt is mixed in an earthen jar with water and yeast, or decaying cheese, and left for a few days at 30° or 40°; the calcium succinate thus obtained is decomposed by dilute sulphuric acid; and the succinic acid is purified by crystallisation from water and by sublimation.

Succinic acid crystallises in colourless, monoclinic prisms, which dissolve in 23 parts of water at 20° and in 4 parts of boiling water: it melts at 180°, and boils at 235°, at the same time undergoing decomposition into water and succinic oxide, or anhydride, $C_4H_4O_3$, or $(C_4H_4O_2)O$. The same compound is formed by the action of phosphorus pentachloride on succinic acid:

$$C_4H_6O_4 + PCl_5 = POCl_3 + 2HCl + C_4H_4O_3.$$

It is a white mass, less soluble in water, but more soluble in alcohol, than succinic acid.

Succinic acid, being bibasic, forms, with monad metals, acid and neutral salts, $C_4H_5MO_4$ and $C_4H_4M_2O_4$, and with dyad metals, neutral salts containing $C_4H_4M''O_4$, and acid salts $C_4H_4M''O_4.C_4H_6O_4$. —There are also a few double succinates, several basic lead-salts, and a hyperacid potassium-salt.

The succinates of the alkali-metals are easily soluble in water. The *calcium salt*, $C_4H_4CaO_4$, is sparingly soluble in water, and separates from a cold solution with $3H_2O$, and from a hot solution with $1H_2O$. On adding ammonium succinate to the solution of a ferric salt, a basic ferric succinate is thrown down as a reddish-brown precipitate.

Succinic acid is distinguished from benzoic acid by not being precipitated from its soluble salts by mineral acids, and by forming a white precipitate with barium chloride, on addition of alcohol and ammonia.

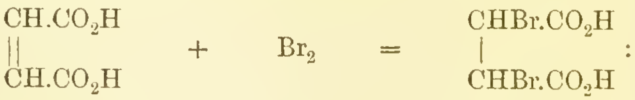
Ethylic succinate, $C_2H_4(CO_2.C_2H_5)_2$, obtained by the action of hydrochloric acid on an alcoholic solution of succinic acid, is a thick oil, insoluble in water, having a specific gravity of 1·072 at 0°, and boiling at 216°.

Succinic chloride, $C_2H_4(CO.Cl)_2$, formed by the action of PCl_5, on excess of succinic acid, is an oil which solidifies at 0°, and boils at 90°.

Bromosuccinic acids.—The mono- and di-brominated acids are formed by heating succinic acid with bromine and water in sealed tubes to 150°–180°.

Monobromosuccinic acid, $C_2H_3Br(CO_2H)_2$, which is the chief product formed when a large quantity of water is used, crystallises in nodular groups of slender needles, easily soluble in water. It melts at 160°, giving off HBr, and being converted into fumaric acid, $C_4H_4O_4$. By boiling with silver oxide and water, it is converted into oxysuccinic or malic acid, $C_2H_3(OH)(CO_2H)_2$.

Dibromosuccinic acid, $C_2H_2Br_2(CO_2H)_2$, is also formed by direct combination of fumaric acid with bromine:



$$\begin{array}{l} CH.CO_2H \\ \| \\ CH.CO_2H \end{array} \quad + \quad Br_2 \quad = \quad \begin{array}{l} CHBr.CO_2H \\ | \\ CHBr.CO_2H \end{array} \quad :$$

further, by heating succinyl chloride with bromine, and decomposing the resulting dibromosuccinyl chloride, $C_2H_2Br_2(COCl)_2$, with water.

This acid crystallises in prisms, sparingly soluble in cold, more freely in hot water.

Its salts are decomposed by boiling with water, the silver salt yielding dioxysuccinic or inactive tartaric acid; the sodium salt, monobromomalic acid; and the barium salt, monobromomaleic acid; thus:

$$C_4H_2Ag_2Br_2O_4 + 2H_2O = 2AgBr + \underset{\text{Tartaric acid.}}{C_4H_6O_6}$$

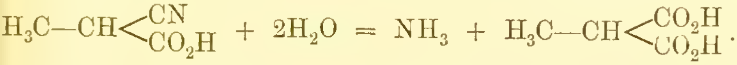
$$C_4H_2Na_2Br_2O_4 + H_2O = NaBr + \underset{\text{Bromomalate.}}{C_4H_4NaBrO_5}$$

$$2C_4H_2BaBr_2O_4 = BaBr_2 + \underset{\text{Bromomaleate}}{(C_4H_2BrO_4)_2Ba}$$

Ethylic dibromosuccinate, $C_2H_2Br_2(CO_2C_2H_5)_2$, melts at 58°, and boils at 140°–150°.

Sulphosuccinic acid, $C_2H_3(SO_3H)(CO_2H)_2$, is a tribasic acid formed by dissolving succinic acid in fuming sulphuric acid, and by the combination of fumaric or maleic acid with the acid sulphites of the alkali-metals.

Isosuccinic or Ethidene-dicarbonic Acid, $H_3C—CH{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$, is prepared from α-chloropropionic acid, through the medium of the cyanogen-derivative:



$$H_3C—CH{<}\begin{matrix}CN\\CO_2H\end{matrix} + 2H_2O = NH_3 + H_3C—CH{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}.$$

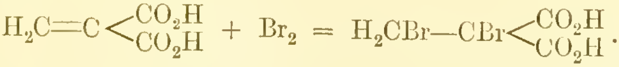
It cannot be prepared from ethidene dibromide, $H_3C—CHBr_2$; for on heating this compound with potassium cyanide and an alkali, a molecular transposition takes place, resulting in the formation of ordinary or ethene-succinic acid.

Isosuccinic acid crystallises in needles soluble in 4 parts of water. It melts at 130°, and is resolved at higher temperatures into propionic acid and carbon dioxide:

$$CH_3—CH(CO_2H)_2 = CO_2 + CH_3—CH_2—CO_2H.$$

The same decomposition takes place on heating the acid with water above 100°; in fact, this mode of decomposition into CO_2 and a monocarbon acid is characteristic of the di-carbon acids in which the two carboxyl-groups are attached to one carbon-atom.

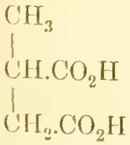
Dibromisosuccinic acid, $C_2H_2Br_2(CO_2H)_2$, is formed by addition of bromine to maleic acid:



$$H_2C{=}C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix} + Br_2 = H_2CBr—CBr{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}.$$

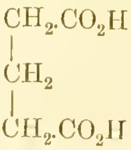
It is crystalline, easily soluble in water, melts at 150°, and is resolved on further heating, or on boiling with water, into HBr, and isobromomaleic acid, $CHBr{=}C(CO_2H)_2$. Sodium amalgam converts it, by molecular transposition, into ordinary succinic acid.

Pyrotartaric Acids, $C_5H_8O_4 = C_3H_6{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$. — Of these acids there are four modifications:



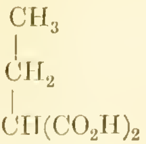
$$\begin{matrix}CH_3\\|\\CH.CO_2H\\|\\CH_2.CO_2H\end{matrix}$$

Pyrotartaric.



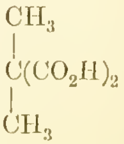
$$\begin{matrix}CH_2.CO_2H\\|\\CH_2\\|\\CH_2.CO_2H\end{matrix}$$

Glutaric.



$$\begin{matrix}CH_3\\|\\CH_2\\|\\CH(CO_2H)_2\end{matrix}$$

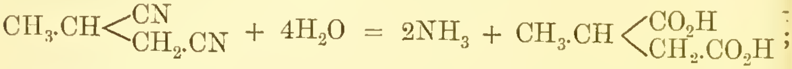
Ethylmalonic.



$$\begin{matrix}CH_3\\|\\C(CO_2H)_2\\|\\CH_3\end{matrix}$$

Dimethyl-malonic.

Pyrotartaric or Methyl-succinic Acid, $CH_3.CH<\begin{smallmatrix}CO_2H\\CH_2.CO_2H\end{smallmatrix}$ is obtained by the dry distillation of tartaric acid, mixed with an equal weight of powdered pumice; synthetically also from propene bromide, through the medium of the cyanide:



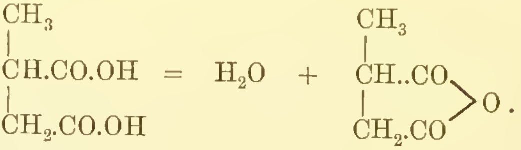
$$CH_3.CH<\begin{matrix}CN\\CH_2.CN\end{matrix} + 4H_2O = 2NH_3 + CH_3.CH<\begin{matrix}CO_2H\\CH_2.CO_2H\end{matrix};$$

also by the action of nascent hydrogen on the three isomeric acids, itaconic, citraconic, and mesaconic:

$$C_5H_6O_4 + H_2 = C_5H_8O_4;$$

and lastly by treating allyl iodide with potassium cyanide, and boiling the resulting nitril with a caustic alkali.

It crystallises in small rhombic prisms, easily soluble in water, alcohol, and ether, melts at 112°, and when rapidly heated is resolved into water and pyrotartaric anhydride, which distils over, and boils at 230°.



$$\begin{matrix}CH_3\\|\\CH.CO.OH\\|\\CH_2.CO.OH\end{matrix} = H_2O + \begin{matrix}CH_3\\|\\CH..CO\\|\\CH_2.CO\end{matrix}\!\!>O.$$

On heating it for a longer time to 200°-210°, or on exposing its aqueous solution, mixed with a uranium-salt, to sunshine, it is restored into CO_2 and butyric acid, $CH_3—CH_2—CH_2—CO_2H$.

Neutral calcium pyrotartrate, $C_5H_6O_4Ca+2H_2O$, and the acid potassium salt $C_5H_7O_4K$, are sparingly soluble in water.

Normal Pyrotartaric Acid, $CH_2<\begin{smallmatrix}CH_2.CO.OH\\CH_2.CO.OH\end{smallmatrix}$, also called glutaric acid, is formed by heating propene cyanide, $CH_2<\begin{smallmatrix}CH_2.CN\\CH_2.CN\end{smallmatrix}$, with strong hydrochloric acid, to 100°, in a sealed tube for three or four hours. The contents of the tube are then evaporated down on a water-bath, treated with absolute alcohol to separate ammonium chloride, and the alcoholic solution is evaporated down, whereupon the acid is left as a thick brown syrup, which very slowly crystallises. It may be purified by conversion into silver salt, and separation therefrom by hydrogen sulphide. The same acid is obtained by heating oxyglutaric acid (*q.v.*), with concentrated hydriodic acid to 120°. It forms large transparent monoclinic crystals, easily soluble in water, melting at 97°, and decomposing above 280° into water and the anhydride, $CH_2<\begin{smallmatrix}CH_2.CO\\CH_2.CO\end{smallmatrix}>O$.

Ethylmalonic Acid, $CH_3.CH_2.CH{<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, is prepared from α-bromobutyric acid (p. 392), through the medium of the cyano-compound:

$$CH_3.CH_2.CH(CN).CO_2H + 2H_2O = NH_3 + CH_3.CH_2.CH{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}.$$

It crystallises in colourless prisms, resembling pyrotartaric acid, and melting, like the latter, at 112°. When heated to 160°, it is resolved into CO_2 and butyric acid. The *calcium salt*, $C_5H_6O_4Ca + H_2O$, forms prisms more soluble in cold than in hot water. The *barium salt* is anhydrous. The *copper salt*, $C_5H_6O_4Cu + H_2O$, crystallises in beautiful tablets.

Dimethyl-malonic Acid, $(CH_3)_2C(CO_2H)_2$, prepared from bromisobutyric acid, is less soluble in water than either of the two preceding acids. It decomposes when melted, but does not yield butyric acid.

Substitution-products of the Pyrotartaric Acids.—Isomeric chloro- and bromo-derivatives of these acids are formed by direct addition of HCl, HBr, and Br_2, to the unsaturated acids, $C_5H_6O_4$, viz., itaconic, citraconic, and mesaconic acids, these products being called respectively *ita-*, *citra-*, and *mesa-* derivatives of the pyrotartaric acids.

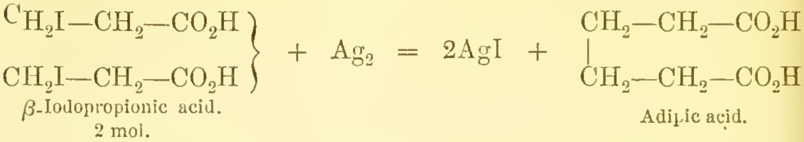
The monochlorinated derivatives, $C_5H_7ClO_4$, are formed by treating the three isomeric acids, $C_5H_6O_4$, with strong hydrochloric acid. They are all three crystalline.—*Itachloropyrotartaric acid* melts at 145°, and when heated with water or alkalis, is converted into itamalic acid, $C_5H_7(OH)O_4$.—*Citrachloropyrotartaric acid* is very unstable, and when heated with water gives up HCl, and passes into mesaconic acid, $C_5H_6O_4$ (p. 354). By boiling with alkalis, it is resolved into CO_2, HCl, and methacrylic acid, $C_4H_6O_2$.—*Mesachloropyrotartaric acid* is more stable than the last, melts at 129°, and is converted by heating with water into mesamalic acid, $C_5H_8O_5$.

The three isomeric dibromopyrotartaric acids differ from one another in their degree of solubility in water. The ita-compound is converted, by boiling the aqueous solution of its sodium salt, into aconic acid, $C_5H_4O_4$. The citra- and mesa-compounds, on the other hand, yield bromocrotonic acid, C_4H_5BrO.

All these chloro-derivatives, and the corresponding bromo- and iodo-pyrotartaric acids, are converted by nascent hydrogen into ordinary pyrotartaric acid.

The constitution of the substituted pyrotartaric acids will be understood from that of the three isomeric acids, $C_5H_6O_4$ (p. 353).

Adipic Acids, $C_6H_{10}O_4 = C_4H_8{<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$.—1. *Normal Adipic acid*, $CO_2H—(CH_2)_4—CO_2H$, originally obtained by the oxidation of fats with nitric acid, is formed synthetically by heating β-iodopropionic acid with finely divided silver:



$$\underset{\substack{\beta\text{-Iodopropionic acid.}\\ \text{2 mol.}}}{\left.\begin{array}{l}CH_2I{-}CH_2{-}CO_2H\\ CH_2I{-}CH_2{-}CO_2H\end{array}\right\}} + Ag_2 = 2AgI + \underset{\text{Adipic acid.}}{\begin{array}{l}CH_2{-}CH_2{-}CO_2H\\ |\\ CH_2{-}CH_2{-}CO_2H\end{array}}$$

It is also produced by the action of nascent hydrogen on hydromuconic acid, $C_6H_8O_4$; by oxidising sebacic acid with nitric acid; and, together with acetic acid and carbon dioxide, by oxidation of phorone with chromic acid:

$$C_8H_{14}O + O_7 = C_6H_{10}O_4 + C_2H_4O_2 + CO_2.$$

This acid crystallises in shining laminæ or prisms, dissolves in 13 parts of cold water, and melts at 148°.

2. *Isoadipic* or *Dimethyl-succinic acid*, $\begin{array}{l}CH_3{-}CH{-}CO_2H\\ \quad\quad\;\; |\\ CH_3{-}CH{-}CO_2H\end{array}$, produced by heating α-bromopropionic acid, $CH_3{-}CHBr{-}CO_2H$, with finely divided silver, forms a thick syrup which does not readily crystallise.

The higher acids of this series are formed by the oxidation of stearic acid, oleic acid, and other acids of the fatty and acrylic series with nitric acid,—succinic acid and some of the lower homologues being generally formed at the same time. The mixed acids thus obtained are separated by fractional crystallisation from ether, the higher members separating out first.

Pimelic Acid, $C_7H_{12}O_4$, is also produced by fusing camphoric acid with potash. It melts at 114°, and dissolves in 40 parts of cold water.

Suberic Acid, $C_8H_{14}O_4$, is most readily obtained by boiling cork with nitric acid. It crystallises in long needles or plates, melts at 140°, and sublimes without decomposition between 150°–160°. It dissolves in 100 parts of cold water, easily in hot water, alcohol, and ether.

An isomeric acid, tetramethylsuccinic acid, $\begin{array}{l}(CH_3)_2C{-}CO_2H\\ \quad\quad\;\; |\\ (CH_3)_2C{-}CO_2H\end{array}$, is formed by heating bromisobutyric acid $(CH_3)_2CBr.CO_2H$, with reduced silver. It melts at 95°, and dissolves in 45 parts of water at 10°.

A third isomeride, diethylsuccinic acid, $\begin{array}{l}C_2H_5.CH.CO_2H\\ \quad\quad\;\; |\\ C_2H_5.CH.CO_2H\end{array}$, is formed in like manner from α-bromobutyric acid, $C_2H_5.CHBr.CO_2H$.

Anchoic Acid, or **Lepargylic Acid,** $C_9H_{16}O_4$, is formed, together with other products, by the action of nitric acid on Chinese wax and on the fatty acids of cocoa-nut oil.—Azelaic acid, obtained by oxidising castor-oil with nitric acid, has the same composition as anchoic acid, but differs so much from it in physical properties, that it must be regarded as an isomeric or allotropic modification.

Sebic or **Sebacic Acid,** $C_{10}H_{18}O_4$, is a constant product of the destructive distillation of oleic acid, olein, and all fatty substances containing those bodies; it is extracted by boiling the distilled matter with water: it is also formed by the action of potash on castor-oil (see p. 158). It forms small pearly crystals resembling those of benzoic acid. It has a faintly acid taste, is but little soluble in cold water, melts when heated, and sublimes unchanged.

Brassylic Acid, $C_{11}H_{20}O_4$, obtained by oxidation of behenolic acid and erucic acid, melts at 1·08°, and is nearly insoluble in water.

Roccellic Acid, $C_{17}H_{32}O_4$, exists in *Roccella tinctoria*, and other lichens of the same genus, also in *Lecanora tartarea*, and is obtained by exhausting the first-mentioned plant with aqueous ammonia, precipitating the filtered liquor with calcium chloride, and decomposing the resulting calcium salt with hydrochloric acid. When purified by solution in ether, it forms white, rectangular, four-sided tabular crystals, melting at 132°, and subliming at 200°, being partially converted at the same time into an oxide, $C_{17}H_{30}O_3$. This acid decomposes carbonates.

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2. **Unsaturated Acids,** $C_nH_{2n-4}O_4$ or $C_nH_{2n-2}\!<\!\begin{smallmatrix}CO_2H\\ CO_2H\end{smallmatrix}$.—This series includes the following groups of isomeric acids:

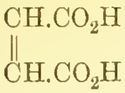
Fumaric and Maleic acids, ...	$C_4H_4O_4$
Itaconic, Citraconic, Mesaconic, and Paraconic acids, ...	$C_5H_6O_4$
Hydromuconic acid, ...	$C_6H_8O_4$.

These acids are capable of taking up two atoms of hydrogen, bromine, and other monad elements, and passing into the saturated acids of the preceding series. A general method of forming them consists in heating the dibrominated derivatives of the acids, $C_nH_{2n-2}O_4$, with solution of potassium iodide; *e.g.*:

$$\underset{\text{Dibromosuccinic.}}{\begin{array}{l}CHBr.CO_2H\\ |\\ CHBr.CO_2H\end{array}} + 2KI = 2KBr + I_2 + \underset{\text{Fumaric.}}{\begin{array}{l}CH.CO_2H\\ \|\\ CH.CO_2H\end{array}}$$

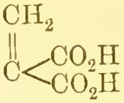
The isomeric modifications of these acids are determined by the structure of the radicles C_nH_{2n-2}, associated with the two carboxyl groups.

Fumaric and **Maleic Acids,** $C_4H_4O_4$,



$$\begin{array}{l} CH.CO_2H \\ \| \\ CH.CO_2H \end{array}$$

Fumaric.



$$\begin{array}{l} CH_2 \\ \| \\ C{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} \end{array}$$

Maleic.

These two acids are produced by the dry distillation of malic acid:

$$C_4H_6O_5 = H_2O + C_4H_4O_4 .$$

When malic acid is heated in a small retort nearly filled with it, it melts, boils, and gives off water, together with maleic acid and maleic anhydride, which pass over into the receiver, and dissolve in the water. After a time, small solid, crystalline scales make their appearance in the boiling liquid, and increase in quantity until the whole becomes solid. The process may now be interrupted, and the contents of the retort, after cooling, treated with cold water: unaltered malic acid is thereby dissolved out, and fumaric acid, which is less soluble, remains behind.

Fumaric acid exists, in the free state, in several plants, as in the common fumitory (*Fumaria officinalis*), Iceland moss (*Cetraria islandica*), and in certain fungi. It is produced also, as above stated, by the action of potassium iodide on dibromosuccinic acid, and from monobromosuccinic and sulphosuccinic acids by fusion with potash.

Fumaric acid forms small, white, crystalline laminæ, which dissolve freely in hot water and alcohol, but require for solution about 200 parts of cold water: it is unchanged by hot nitric acid. When heated in a current of air, it sublimes, but by distillation in a retort, it is resolved in water and maleic anhydride, $C_4H_2O_3$. Similar differences are often observed in the behaviour of organic bodies of small volatility, according as they are heated in close vessels or in a current of air. Fumaric acid is converted by *sodium amalgam*, *hydriodic acid*, and other hydrogenising agents, into ordinary succinic acid. It unites, in presence of water, with metallic *zinc*, forming succinate of zinc, $C_4H_4O_4Zn$.

Fumaric acid forms acid and neutral metallic salts. The *calcium* and *barium salts* are anhydrous. The *silver salt*, $C_4H_2O_4Ag_2$, is quite insoluble in water. The *ethylic ether*, $C_4H_2O_4(C_2H_5)_2$, is a liquid boiling at 225°.

Maleic Acid, $H_2C{=}C{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}$, crystallises in large prisms or tables, very soluble in water, alcohol, and ether, and having a strong acid taste and reaction. It is converted by heat into fumaric acid, by nascent hydrogen into succinic acid, and by bromine into dibromisosuccinic acid, $H_2BrC{-}CBr(CO_2H)_2$. Its aqueous solution dissolves zinc without evolution of hydrogen, forming maleate and succinate of zinc:

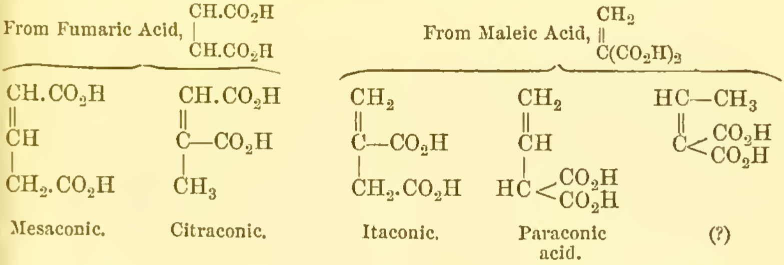
$$3C_4H_4O_4 + 2Zn = C_4H_2O_4Zn + (C_4H_4O_2)_2H_2Zn .$$

Maleic anhydride, $C_4H_2O_3$, crystallises in large laminæ or needles, melts at 57°, boils without decomposition at 196°, and is converted by water into maleic acid.

Maleic and fumaric acids are resolved by electrolysis of the concentrated solutions of their sodium salts into carbon dioxide, hydrogen, and acetylene:

$$C_2H_2(CO_2H)_2 = C_2H_2 + 2CO_2 + H_2 .$$

Acids, $C_5H_6O_4 = C_3H_4{<}\substack{CO_2H \\ CO_2H}$.—Theory indicates the existence of five isomeric acids of this form, and of these four are known, viz., citraconic and mesaconic acids, which may be derived from fumaric acid by interpolation of CH_2, and itaconic and paraconic acids, derivable in like manner from maleic acid:



Citraconic and itaconic acids are produced by the action of heat on citric acid. When crystallised citric acid is heated in a retort, it first melts in its water of crystallisation, and then boils, giving off water. Afterwards, at about 175°, vapours of acetone distil over, and a copious disengagement of carbon monoxide takes place. At this time the residue in the retort consists of aconitic acid. If the distillation be still continued, carbon dioxide is given off, and itaconic acid crystallises in the neck of the retort. If these crystals be repeatedly distilled, an oily mass of citraconic oxide or anhydride is obtained, which no longer solidifies. These decompositions are represented by the following equations:—

$$\underset{\text{Citric acid.}}{C_6H_8O_7} - H_2O = \underset{\text{Aconitic acid.}}{C_6H_6O_6}; \quad \underset{\text{Aconitic acid.}}{C_6H_6O_6} - CO_2 = \underset{\text{Itaconic acid.}}{C_5H_6O_4};$$

$$\underset{\text{Itaconic acid.}}{C_5H_6O_4} - H_2O = \underset{\text{Citraconic anhydride.}}{C_5H_4O_3}$$

The citraconic anhydride when exposed to the air absorbs moisture, and is converted into crystallised citraconic acid, $C_5H_6O_4$.

Mesaconic acid is produced by boiling itaconic acid with weak nitric acid. These three isomeric acids are all converted by nascent hydrogen into pyrotartaric acid, $C_5H_8O_4$. They also take up a molecule of HBr, HCl, HI, forming isomeric monobromopyrotartaric acids, $C_5H_7BrO_4$, &c., or of bromine, Br_2, forming isomeric dibromopyrotartaric acids. Itaconic and citraconic acids are, however, more inclined to these transformations than mesaconic acid, which is altogether a more stable compound.

On subjecting their potassium salts to electrolysis, the three acids are decomposed, yielding a hydrocarbon C_3H_4, according to the equation:

$$C_3H_4(CO_2H)_2 = C_3H_4 + 2CO_2 + H_2.$$

Now, citraconic acid thus treated yields ordinary allylene, $CH{\equiv}C{-}CH_3$, whereas itaconic acid yields iso-allylene or allene, $CH_2{=}C{=}CH_2$, results which are in accordance with the formulæ above given for these acids. Mesaconic acid likewise yields allylene, as might be expected, since the hydrocarbon $CH{=}CH{-}CH_2$ cannot exist.

Itaconic Acid is most easily prepared by heating citraconic anhydride with water to 130°–140°. It crystallises in rhombic octohedrons, dissolves in 17 parts of water at 10°, melts at 161°, and is resolved by distillation into water and citraconic anhydride.

Citraconic Acid crystallises in four-sided prisms, melting at 80°. It is much more soluble in water than itaconic acid, and deliquesces on exposure to the air. Its anhydride, $C_5H_4O_3$, forms an oily liquid, which easily recombines with water to form the acid.

Mesaconic Acid forms shining prisms sparingly soluble in water, melts at 208°, and sublimes without decomposition. It is most readily obtained by the action of heat on citrachloropyrotartaric acid.

Paraconic Acid is formed, together with itamalic acid, $C_5H_8O_5$, by heating itachloropyrotartaric acid, $CH_2Cl - CH.CO_2H - CH_2.CO_2H$, with water. It is easily soluble in water, melts at 70°, and is resolved by distillation into water and citraconic anhydride. It unites with HBr, forming itabromopyrotartaric acid. When heated with alkalis it takes up water, and forms itamalic acid, $C_5H_6O_5$.

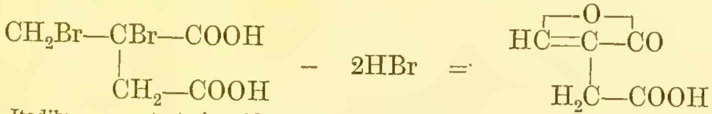
The constitution of paraconic acid is probably represented either by the fourth or the fifth formula above given; but there is at present no means of deciding between the two. Moreover, it is not easy to see how an acid having its two carboxyl-groups associated with the same carbon-atom could be formed from itabromopyrotartaric acid, unless the reaction were accompanied by molecular transposition.

Hydromuconic Acid, $C_6H_8O_4 = C_4H_8(CO_2H)_2$, produced by the action of sodium-amalgam on dichloromuconic acid, $C_6H_6Cl_2O_4$, crystallises in large prisms, slightly soluble in cold water, and melting at 195°. It is converted by sodium-amalgam into adipic acid,

$C_6H_{10}O_4$, and unites with bromine, forming dibromadipic acid, $C_6H_8Br_2O_4$.

3. Unsaturated Acids, $C_nH_{2n-6}O_4$.

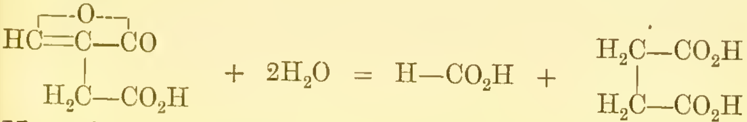
Aconic Acid, $C_5H_4O_4$.—This acid is formed by boiling itadibromopyrotartaric acid with caustic soda. It is very soluble in water, alcohol, and ether, and crystallises from the alcoholic solution in foliate groups of shining needles, melting at 154°. From its origin it might be expected to be a bibasic acid; but it is really monobasic, its silver-salt being $C_5H_3O_4Ag$, and its barium salt $(C_5H_3O_4)_2Ba$. This may perhaps be explained by regarding the acid as an anhydro-acid similar to dilactic acid, its mode of formation being represented by the following equation:



$$\begin{array}{l}\mathrm{CH_2Br{-}CBr{-}COOH}\\ \qquad\ |\\ \qquad \mathrm{CH_2{-}COOH}\end{array} \;-\; 2HBr \;=\; \begin{array}{l}\quad\overbrace{}^{O}\\ \mathrm{HC{=}C{-}CO}\\ \qquad |\\ \quad\mathrm{H_2C{-}COOH}\end{array}$$

Itadibromopyrotartaric acid. Aconic acid.

By boiling with baryta-water, aconic acid is resolved into formic and succinic acids:



$$\begin{array}{l}\quad\overbrace{}^{O}\\ \mathrm{HC{=}C{-}CO}\\ \qquad |\\ \quad\mathrm{H_2C{-}CO_2H}\end{array} + 2H_2O = H{-}CO_2H + \begin{array}{l}\mathrm{H_2C{-}CO_2H}\\ \quad |\\ \mathrm{H_2C{-}CO_2H}\end{array}$$

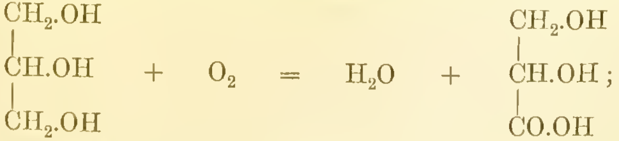
Muconic Acid, $C_6H_6O_4$, formed in like manner from dibromadipic acid, forms large crystals melting at 100°. It is monobasic, like aconic acid, and is probably constituted in a similar manner. By boiling with baryta-water it is resolved into acetic and succinic acids.

Triatomic Acids.

1. MONOBASIC, $C_nH_{2n}O_4$.

These acids are derived from the triatomic alcohols, $C_nH_{2n+2}O_3$ (glycerins) by substitution of O for H_2, in the same manner as the acids of the lactic series, $C_nH_{2n}O_3$, from the glycols, $C_nH_{2n+2}O_2$. There is, however, but one acid of the series at present known, viz.:

Glyceric Acid, $C_3H_6O_4$ (dioxypropionic acid), which is formed by the gradual oxidation of glycerin with nitric acid:



$$\begin{array}{l}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH.OH}\\ |\\ \mathrm{CH_2.OH}\end{array} + O_2 = H_2O + \begin{array}{l}\mathrm{CH_2.OH}\\ |\\ \mathrm{CH.OH;}\\ |\\ \mathrm{CO.OH}\end{array}$$

also by heating glycerin to 100° in a sealed tube, with bromine and water:

$$C_3H_8O_3 + 2Br_2 + H_2O = 4HBr + C_3H_6O_4.$$

To prepare it, nitric acid (specific gravity 1·5), is poured through a long-necked funnel to the bottom of a tall glass jar containing glycerin, diluted with an equal bulk of water (100 grains of glycerin, 100 of water, and 100 to 150 of red nitric acid, are good proportions). The two layers of liquid gradually mix, and assume a blue colour, and the oxidation of the glycerin proceeds, accompanied by copious evolution of gas; if the liquid becomes too hot, the action must be moderated by external cooling. When the action is completed, which takes five or six days, the acid liquid is evaporated to a syrup, diluted with water, saturated at the boiling heat with chalk and a small quantity of milk of lime, and then filtered. The concentrated filtrate deposits calcium glycerate in warty crusts, from which the glyceric acid may be separated by boiling with oxalic acid. The liquid filtered from the calcium oxalate is boiled with lead oxide to remove any excess of oxalic acid, then treated with hydrogen sulphide to precipitate the dissolved lead, and the filtered liquid is evaporated over the water-bath.

Glyceric acid when concentrated is a colourless, uncrystallisable syrup, very soluble in water and in alcohol. Heated above 140°, it is decomposed, yielding water, pyruvic acid, and pyrotartaric acid. By fusion with potash it is resolved into acetic and formic acids; by boiling with aqueous potash, it yields oxalic and lactic acids, and by the action of phosphorus iodide it is converted into β-iodopropionic acid.

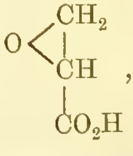
The metallic glycerates are soluble in water, and crystallise well. They are not reddened by ferrous salts, and are thereby distinguished from the pyruvates, from which they differ only by the elements of water. The *calcium salt*, $(C_3H_5O_4)_2Ca + 2H_2O$, usually crystallises in nodular groups of needles, easily soluble in water: the lead salt $(C_3H_5O_4)_2Pb$, is but slightly soluble in water.

The *ethylic ether*, $C_3H_5O_4.C_2H_5$, obtained by heating glycerin with absolute alcohol, is a thick liquid, having a specific gravity of 1·193 at 0°, and boiling at 230°–240°.

Amidoglyceric acid, $CH_2.NH_2—CH.OH—CO_2OH$, or serine, is obtained by boiling sericin or silk-gelatin (*q.v.*), with dilute sulphuric acid. It forms hard crystals, soluble in water, but insoluble in alcohol and ether. It unites both with acids, and with bases. Nitrous acid converts it into glyceric acid.

Anhydrides of Glyceric Acid.

Pyruvic or **Pyroracemic Acid,** $C_3H_4O_3 =$



$$O\left\langle\begin{array}{l}CH_2\\ |\\ CH\\ |\\ CO_2H\end{array}\right.$$

, or $CO<\substack{CH_3\\ CO_2H}$.—This anhydro-acid is formed, together with other products, by the dry distillation of glyceric, tartaric, or racemic acid:

$$C_3H_6O_4 = C_3H_4O_3 + H_2O$$
$$C_4H_6O_6 = C_3H_4O_3 + CO_2 + H_2O;$$

and is obtained pure by redistilling the product several times, and collecting apart the portion which passes over between 165° and 170°. It is a yellowish liquid, easily soluble in water, alcohol, and ether; smells like acetic acid, and boils with partial decomposition at 165°–170°. It is monobasic, and forms salts which crystallise well, provided that heat is avoided in their preparation; but their solutions, if evaporated by heat, leave gummy uncrystallisable salts, which yield a syrupy non-volatile modification of the acid, likewise obtained when an aqueous solution of the original acid is evaporated by heat. This syrupy acid, which is probably a polymeric modification, is resolved by heat into carbon dioxide and pyrotartaric acid, $2C_3H_4O_3 = CO_2 + C_5H_8O_4$.

Pyruvic acid is converted by nascent hydrogen into ordinary lactic acid, $CH_3—CHOH—COOH$, and may therefore be regarded as a ketonic acid related to lactic acid in the same manner as dimethylketone (acetone) to secondary propyl alcohol, as represented by the second of the constitutional formulæ above given:

$CH_3—CO—CH_3$ Dimethyl ketone.	$CH_3—CHOH—CH_3$ Pseudopropyl alcohol.
$CH_3—CO—COOH$ Pyruvic acid.	$CH_3—CHOH—COOH$ α-Lactic acid.

The reaction, however, agrees equally well with the first formula, which represents pyruvic acid as an anhydride of glyceric acid, from which it is formed by actual dehydration.

Pyruvic acid is converted by phosphorus pentachloride into dichloropropionic chloride, $CH_2Cl—CHCl—COCl$; by hydrochloric acid at 100° into carbon dioxide and pyrotartaric acid; by oxidising agents into oxalic acid; by boiling with baryta-water into uvitic acid, $C_9H_8O_4 = C_6H_3 \left\{ \begin{array}{l} CH_3 \\ (CO_2H)_2 \end{array} \right.$, an acid belonging to the aromatic group.

The pyruvates crystallise well, provided that heat is avoided in their preparation. The *sodium salt*, $C_3H_3O_3Na$, forms large anhydrous prisms. The *lead salt*, $(C_3H_3O_3)_2Pb$, is a crystalline precipitate. The *silver salt* is also crystalline.

Oxypyruvic or **Carbacetoxylic Acid**, $C_3H_4O_4$ or $CH_2OH—CO—CO_2H$, isomeric with malonic acid, is formed by heating β-chloropropionic acid with excess of silver oxide:

$$CH_2Cl.CH_2.CO_2H + 3Ag_2O = CH_2OH.CO.CO_2Ag + AgCl + 2Ag_2 + H_2O.$$

It forms a syrup, easily soluble in water and in ether. It is monobasic; its *barium salt* crystallises in spherical nodules; the *lead salt* incrusts; the *zinc salt* in shining scales.

The acid is converted by nascent hydrogen into glyceric acid, and by hydriodic acid at 200° into pyruvic acid.

TRIATOMIC AND BIBASIC ACIDS,

$$C_nH_{2n-2}O_5, \text{ or } C_nH_{2n-1}(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix} .$$

The acids of this series may be formed from those of the oxalic or succinic series, $C_nH_{2n}(CO_2H)_2$, by substitution of OH for H. Four of them are at present known, viz.:

Tartronic acid,	$C_3H_4O_5$.	Oxypyrotartaric acid,	$C_5H_8O_5$.
Malic acid,	$C_4H_6O_5$.	Oxyadipic acid,	$C_6H_{10}O_5$.

Tartronic Acid, $CH(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$ (oxymalonic acid), is formed by the action of nascent hydrogen on mesoxalic acid (p. 344):

$$CO(CO_2H)_2 + H_2 = CHOH(CO_2H)_2 ;$$

also by spontaneous decomposition of dinitrotartaric acid (p. 367), when its aqueous solution is left to evaporate, the decomposition being attended with evolution of carbon dioxide and nitrogen dioxide :

$$C_2H_2(O.NO_2)_2(CO_2H)_2 = CHOH(CO_2H)_2 + CO_2 + N_2O_2 .$$

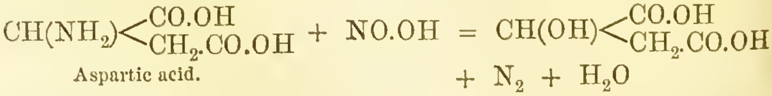
Tartronic acid crystallises in large prisms, which melt at 175°, and are resolved at higher temperatures into carbon dioxide, water, and glycollide :

$$C_3H_4O_5 = CO_2 + H_2O + C_2H_2O_2 .$$

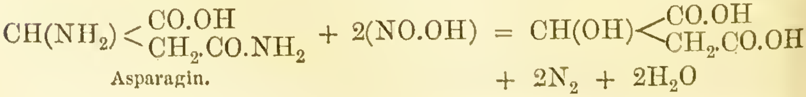
Malic Acid, $C_4H_6O_5 = C_2H_3(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = CH(OH) < \begin{matrix} CO_2H \\ CH_2.CO_2H \end{matrix}$, *Oxysuccinic acid.*—This acid is formed synthetically by the action of moist silver oxide on bromosuccinic acid :

$$C_2H_3Br(CO_2H)_2 + AgOH = AgBr + C_2H_3OH(CO_2H)_2 .$$

It is also produced by deoxidation of tartaric acid, $C_4H_6O_6$, with hydriodic acid, and by the action of nitrous acid on aspartic acid, $C_4H_7NO_4$ (amidosuccinic acid), or on asparagin, $C_4H_8N_2O_3$, which is the amide of the latter :



$$\underset{\text{Aspartic acid.}}{CH(NH_2) < \begin{matrix} CO.OH \\ CH_2.CO.OH \end{matrix}} + NO.OH = CH(OH) < \begin{matrix} CO.OH \\ CH_2.CO.OH \end{matrix} + N_2 + H_2O$$



$$\underset{\text{Asparagin.}}{CH(NH_2) < \begin{matrix} CO.OH \\ CH_2.CO.NH_2 \end{matrix}} + 2(NO.OH) = CH(OH) < \begin{matrix} CO.OH \\ CH_2.CO.OH \end{matrix} + 2N_2 + 2H_2O$$

Malic acid is the acid of apples, pears, and various other fruits; it is often associated with citric acid. It may be advantageously prepared from the juice of the garden rhubarb, in which it exists in large quantity, accompanied by acid potassium oxalate. The rhubarb stalks are peeled, and ground or grated to pulp, which is subjected to pressure. The juice is heated to the boiling point, neutralised with potassium carbonate, and mixed with calcium acetate: insoluble calcium acetate then falls, and may be removed by filtration. To the clear and nearly colourless liquid, solution of lead acetate is added as long as a precipitate continues to be produced, and the lead malate is collected on a filter, washed, diffused through water, and decomposed by sulphuretted hydrogen. The filtered liquid is carefully evaporated to the consistence of a syrup, and left in a dry atmosphere till it becomes converted into a solid and somewhat crystalline mass of malic acid. From the berries of the mountain-ash (*Sorbus aucuparia*), in which malic acid is likewise present in considerable quantity, especially at the time they begin to ripen, the acid may be prepared by the same process.

Malic acid crystallises in groups of colourless prisms, slightly deliquescent and very soluble in water; alcohol also dissolves it. The aqueous solution has an agreeable acid taste: it becomes mouldy and spoils by keeping.

Malic acid, as it exists in plants, and as obtained from active tartaric acid, from asparagin, or from aspartic acid produced from the latter, exerts a rotatory action on polarised light; $[\alpha] = -5°$; but by the action of nitrous acid on inactive aspartic acid (resulting from the decomposition of fumarimide), Pasteur has obtained a modification of malic acid which is optically inactive. Malic acid formed from succinic acid is also inactive.

Malic acid when heated gives off water at 130°, and at 175° a distillate of maleic acid and maleic anhydride, while fumaric acid remains behind (p. 352). By slow oxidation with a cold solution of potassium chromate, it is converted into maleic acid:

$$C_4H_6O_5 + O_2 = CO_2 + H_2O + C_3H_4O_4.$$

Nitric acid readily converts it into oxalic acid, with evolution of carbon dioxide.

By the action of reducing agents, most readily by heating with strong hydriodic acid, malic acid is reduced to succinic acid; also by fermentation of its calcium salt in contact with putrefying cheese, acetic acid and carbon dioxide being also produced:

$$3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + H_2O.$$

The sodium salt of bromomalic acid, $C_4H_5BrO_5$, obtained by boiling an aqueous solution of sodium dibromosuccinate, $(C_4H_3NaBr_2O_4)$, is converted by boiling with lime-water into the calcium-salt of tartaric acid, $C_4H_6O_6$:

$$C_4H_5BrO_5 + H_2O = HBr + C_4H_6O_6.$$

Malic acid forms both acid and neutral salts. Those formed from the optically active acid are likewise active, some being dextro-, others levorotatory. The most characteristic of the malates are *acid ammonium malate*, $C_4H_5(NH_4)O_5$, which crystallises remarkably well, and *lead malate*, $C_4H_4PbO_5.3$ aq., which is insoluble in pure water, but dissolves to a considerable extent in warm dilute acids, and separates on cooling in brilliant silvery crystals containing water. By this character the acid may be distinguished. *Acid calcium malate*, $C_4H_4O_5Ca.C_4H_6O_5 + 8H_2O$, is also a very beautiful salt, freely soluble in warm water. It is prepared by dissolving the sparingly soluble *neutral* malate in hot dilute nitric acid, and leaving the solution to cool.

Diethylic malate, $C_4H_4(C_2H_5)_2O_5$, is a liquid which is partially decomposed by distillation, and is converted by acetyl chloride into diethylic acetomalate, $C_2H_3(OC_2H_3O)<\begin{smallmatrix}CO_2C_2H_5\\CO_2C_2H_5\end{smallmatrix}$.

Oxypyrotartaric Acid, $C_5H_8O_5 = C_3H_5(OH)<\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, is produced by boiling dicyanhydrin, $C_3H_5(OH)(CN)_2$ (p. 182) with alkalis. It forms crystals, easily soluble in water, alcohol, and ether, and melting at 135°.

Isomeric with it are four bibasic acids of unknown structure, called itamalic, citramalic, mesamalic, and oxyglutaric acids.

Ita- and mesamalic acids are formed by boiling the corresponding chloropyrotartaric acids (p. 349) with water or solution of sodium carbonate:

$$C_3H_5Cl(CO_2H)_2 + H_2O = HCl + C_3H_5(OH)(CO_2H)_2.$$

Both form deliquescent crystals, melting at 60°.

Citramalic acid is produced by the action of zinc on chlorocitramalic acid, $C_5H_7ClO_5$ (formed by addition of hypochlorous acid, ClOH, to citraconic acid, $C_5H_6O_4$). It is a deliquescent mass.

Oxyglutaric acid, $C_5H_7(OH)O_4$, produced by the action of nitrous acid on amidoglutaric acid, $C_5H_7(NH_2)O_4$, crystallises with difficulty, and is converted by hydriodic acid into glutaric acid (p. 348).

Amidoglutaric acid, or *Glutamic acid*, $C_5H_7(NH_2)O_4 = C_3H_5(NH_2)<\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, occurs, together with aspartic acid, in the molasses of sugar-beet, and is formed by boiling albuminous bodies with dilute sulphuric acid. It forms shining rhombic octohedrons, moderately soluble in water, insoluble in alcohol and ether, melting with partial decomposition at 140°. It unites both with bases and with acids, and is converted by nitrous acid into oxyglutaric acid.

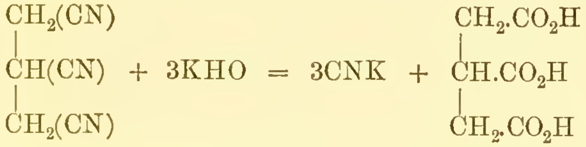
Oxyadipic Acid, $C_6H_{10}O_5 = C_4H_7(OH){<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, is a deliquescent mass formed by the action of moist silver oxide on monobromadipic acid.

Oxymaleic Acid, $C_4H_4O_5 = C_2H(OH){<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$ is an unsaturated triatomic and bibasic acid, produced by the action of silver oxide on bromomaleic acid (p. 352). It crystallises in slender needles, easily soluble in water, alcohol, and ether. An acid isomeric with it is formed from bromisomaleic acid.

TRIATOMIC AND TRIBASIC ACIDS.

Only one saturated acid of this group is known, viz.:

Tricarballylic Acid, $C_6H_8O_6 = C_3H_5(CO_2H)_3$, which is produced: 1. By heating allyl tribromide, $CH_2Br—CHBr—CH_2Br$, with potassium cyanide, and decomposing the resulting tricyanhydrin with potash:



$$\begin{array}{l} CH_2(CN) \\ | \\ CH(CN) \\ | \\ CH_2(CN) \end{array} + 3KHO = 3CNK + \begin{array}{l} CH_2.CO_2H \\ | \\ CH.CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

2. By the action of sodium-amalgam on aconitic acid, $C_6H_6O_6$. 3. By reduction of citric acid, $C_6H_8O_7$, with hydriodic acid.

Tricarballylic acid crystallises in colourless rhombic prisms, easily soluble in water and alcohol, slightly soluble in ether. The tricarballylates of the alkali-metals are easily soluble in water, the rest insoluble or sparingly soluble. The *ethylic ether*, $C_3H_5(CO.OC_2H_5)_3$, is a liquid boiling between 295° and 305°.

The following tribasic acids are unsaturated compounds:

Aconitic Acid, $C_6H_6O_6 = C_6H_3(CO_2H)_3$, exists in monk's-hood (*Aconitum Napellus*), and other plants of the same genus, also in *Equisetum fluviatile*, and is one of the products obtained by the dehydration of citric acid (p. 353): $C_6H_8O_7 - H_2O = C_6H_6O_6$.

When crystallised citric acid is heated in a retort till it begins to become coloured, and to undergo decomposition, and the fused, glassy product, after cooling, is dissolved in water, aconitic acid remains as a white, confusedly crystalline mass, which may be purified by converting it into a lead salt, and decomposing the latter with hydrogen sulphide.

Aconitic acid crystallises in small laminæ, very soluble in water, alcohol, and ether. It melts at 140°, and decomposes at a higher temperature into carbon dioxide, itaconic acid, and citraconic anhydride. Nascent hydrogen converts it into tricarballylic acid.

Aconitic acid forms three series of salts. The *tertiary lead-*

salt, $(C_6H_3O_6)_2Pb_3$, is insoluble in water. The *calcium salt*, $(C_6H_3O_6)_2Ca_3 + 6H_2O$, which is sparingly soluble, occurs abundantly in the expressed juice of monk's-hood; the magnesium salt in that of *Equisetum*. The *ethylic ether*, $C_6H_3O_6(C_2H_5)_3$, is a liquid boiling at about 236°.

The isomeric acid, aceconitic acid, formed by the action of sodium on ethylic monobromacetate, crystallises in slender needles, and forms salts differing in some respects from the aconitates.

Chelidonic Acid, $C_7H_4O_6 = C_4H(CO_2H)_3$, occurs as a calcium salt, together with malic and fumaric acids, in *Chelidonium majus*, and is extracted by boiling the juice, filtering, adding nitric acid, precipitating with lead nitrate, and decomposing the resulting lead salt with hydrogen sulphide. It crystallises in silky needles containing 1 molecule of H_2O, sparingly soluble in cold water and alcohol. It is decomposed by bromine-water, yielding oxalic acid, bromoform, and pentabromacetone, C_3HBr_5O.

Meconic Acid, $C_7H_4O_7 = C_4HO(CO_2H)_3$ (oxychelidonic acid), is a tribasic acid existing in opium. To prepare it, the liquid obtained by exhausting opium with water, is neutralised with powdered marble and precipitated by calcium chloride; and the calcium meconate thus precipitated is suspended in warm water and treated with hydrochloric acid; on cooling, impure meconic acid crystallises, and may be purified by repeated treatment with hydrochloric acid. The pure acid crystallises in mica-like plates, easily soluble in boiling, difficultly soluble in cold water, soluble likewise in alcohol. The crystals contain $C_7H_4O_7 + 3H_2O$, and give off their water at 100°; the dehydrated acid melts at 150°.

Meconic acid forms three series of salts. There are two *silver meconates*, one yellow, containing $C_7HAg_3O_7$; the other white, consisting of $C_7H_2Ag_2O_7$. Meconic acid produces a deep red colour with ferric salts. By the action of sodium-amalgam it is converted into hydromeconic acid, $C_7H_{10}O_7$.

Comenic Acid, $C_6H_4O_5$, is a product of decomposition of meconic acid. When an aqueous, or, better, a hydrochloric solution of meconic acid is boiled, carbon dioxide is evolved, and the solution now contains comenic acid, which crystallises on cooling, being very difficultly soluble in cold water. The same acid may be obtained by heating meconic acid to 200°. It is bibasic: its formation is represented by the equation $C_7H_4O_7 = C_6H_4O_5 + CO_2$.

Pyromeconic or *Pyrocomenic Acid*, $C_5H_4O_3$, is a monobasic acid, formed by submitting either comenic or meconic acid to dry distillation, one molecule of carbon dioxide being evolved in the former case and two in the latter.

Pyrocomenic acid is a weak acid; it is soluble in water and alcohol: from these solutions it crystallises in long colourless needles, which melt at 120°, and begin to sublime at the boiling point of water. Both comenic and pyrocomenic acids exhibit the red coloration with ferric salts.

Tetratomic Acids.

These acids may be derived from tetratomic alcohols by substitution of one, two, three, or four atoms of oxygen for a corresponding number of hydrogen molecules:

$$\begin{array}{ccc}
CH_2OH & CH_2OH & COOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CHOH & CHOH & CHOH \\
| & | & | \\
CH_2OH & COOH & COOH \\
\text{Erythrite.} & \text{Erythritic acid} & \text{Tartaric acid} \\
 & \text{(monobasic).} & \text{(bibasic).}
\end{array}$$

Only one tetratomic acid has, however, been actually formed by oxidation of the corresponding alcohol, namely, erythritic acid, $C_4H_8O_5$, from erythrite, $C_4H_{10}O_4$.

The known tetratomic acids belonging to the fatty group are—

Erythritic acid,	$C_4H_8O_5$	monobasic.
Dioxymalonic,	$C_3H_4O_6$	bibasic.
Tartaric,	$C_4H_6O_6$	
Homotartaric,	$C_5H_8O_6$	
Citric,	$C_6H_8O_7$	tribasic

Erythritic Acid, $C_4H_8O_5 = C_3H_4(OH)_3.CO_2H$, formed by the oxidation of erythrite, $C_4H_{10}O_4$ (p. 186), in aqueous solution in contact with platinum black, is a deliquescent crystalline mass, and is capable of forming salts containing 2 equivalents of metal.

Dioxymalonic Acid, $C_3H_4O_6 = C(OH)_2{<}^{CO_2H}_{CO_2H}$, formed by the action of moist silver oxide or dibromomalonic acid, is probably identical with the hydrate of mesoxalic acid (p. 344).

Tartaric Acid, $C_4H_6O_6 = \begin{array}{l} CHOH—CO_2H \\ | \\ CHOH—CO_2H \end{array} = C_2H_2\left\{\begin{array}{l}(OH)_2 \\ (CO_2H)_2\end{array}\right.$

—This formula includes four bibasic acids, distinguished from one another by certain physical properties, especially by their crystalline forms, and their action on polarised light—namely, Dextrotaric acid, which turns the plane of polarisation to the right; Levotartaric acid, which turns it to the left with equal force; Paratartaric or Racemic acid, which is optically inactive, and separable into equal quantities of dextro- and levotartaric acids; and an inactive variety of tartaric acid, which is not thus separable.

1. DEXTROTARTARIC or ORDINARY TARTARIC ACID.—This is the acid of grapes, tamarinds, pine-apples, and several other fruits, in which it occurs in the state of an acid potassium-salt; calcium tartrate is also occasionally met with. The tartaric acid of commerce is wholly prepared from *tartar* or *argol*, an impure acid potassium tartrate, deposited from wine, or rather from grape-juice in the act of fermentation. This substance is purified by solution in hot water, with the aid of a little pipe-clay and animal charcoal, to remove the colouring matter of the wine, and subsequent crystallisation: it then constitutes *cream of tartar*, and serves for the preparation of the acid. The salt is dissolved in boiling water, and powdered chalk is added as long as effervescence is excited, or the liquid exhibits an acid reaction; calcium tartrate and neutral potassium tartrate are thereby produced, and the latter is separated from the former, which is insoluble, by filtration. The solution of potassium tartrate is then mixed with excess of calcium chloride, which throws down all the remaining acid in the form of calcium-salt; this is washed and added to the former portion, and the whole is digested with a sufficient quantity of dilute sulphuric acid to withdraw the base, and liberate the tartaric acid. The filtered solution is cautiously evaporated to a syrupy consistence, and left to crystallise in a warm place. Liebig found that tartaric acid is artificially produced by the action of nitric acid upon milk sugar.

Tartaric acid forms colourless, transparent monoclinic prisms often of large size; they are permanent in the air, and inodorous; they dissolve with great facility in water, both hot and cold, and are soluble also in alcohol. The solution reddens litmus strongly, and has a pure acid taste. The aqueous solution, as above mentioned, exhibits right-handed polarisation. This solution is gradually spoiled by keeping. The crystallised acid melts at 135°, is converted at 170° into optically inactive mesotartaric acid, and when heated for some time to 180° gives off water, and yields anhydrides (p. 367). Tartaric acid is consumed in large quantities by the calico-printer, being employed to evolve chlorine from solution of bleaching powder, in the production of white or *discharged* patterns upon a coloured ground.

Tartrates.—Tartaric acid being tetratomic and bibasic, has only two hydrogen atoms replaceable by metals, the other two being replaceable by alcoholic or acid radicles. With monad metals it forms acid and neutral salts, $C_4H_5M'O_6$, and $C_4H_4M_2O_6$; with dyad metals, neutral salts, $C_4H_4M''O_6$, and double salts, like *bario-potassic tartrate*, $C_4H_4BaO_6.C_4H_4K_2O_6$. With triad metals it forms a peculiar class of salts, best known in the case of the *antimony-salt* (p. 365).

Potassium Tartrates.—The *neutral salt*, $C_4H_4K_2O_6$, may be obtained by neutralising cream of tartar with chalk, as in the preparation of the acid, or by saturating cream of tartar with potassium carbonate ; it is very soluble, and crystallises with difficulty in right rhombic prisms, which are permanent in the air, and have a bitter, saline taste. The *acid salt*, or *cream of tartar*, $C_4H_5KO_6$, the origin and preparation of which have been already described, forms irregular groups of small transparent or translucent prismatic crystals which grate between the teeth. It dissolves pretty freely in boiling water, but the greater part separates as the solution cools, leaving about $\frac{1}{60}$ or less dissolved in the cold liquid. The salt has an acid reaction and a sour taste. When exposed to heat in a close vessel, it is decomposed, with evolution of inflammable gas, leaving a mixture of finely divided charcoal and pure potassium carbonate, from which the latter may be extracted by water. Cream of tartar is almost always produced when tartaric acid in excess is added to a moderately strong solution of a potassium-salt, and the whole agitated.

Sodium Tartrates.—Two of these salts are known—a *neutral salt*, $C_4H_4Na_2O_6+2aq.$; and an *acid salt*, $C_5H_5NaO_6+aq.$ Both are easily soluble in water, and crystallisable. Tartaric acid and sodium bicarbonate form the ordinary effervescing draughts.

Potassium and Sodium tartrate; Rochelle or *Seignette salt*, $C_4H_4KNaO_6+4$ aq.—This beautiful salt is made by neutralising a hot solution of cream of tartar with sodium carbonate, and evaporating to the consistence of thin syrup. It separates in large, transparent rhombic prisms with hemihedral faces ; they effloresce slightly in the air, and dissolve in $1\frac{1}{2}$ parts of cold water. Acids precipitate cream of tartar from the solution. Rochelle salt has a mild saline taste, and is used as a purgative.

Ammonium Tartrates.—The *neutral tartrate* is a soluble and efflorescent salt, containing $C_4H_4(NH_4)_2O_6+aq.$ The *acid tartrate*, $C_4H_5(NH_4)O_6$, closely resembles ordinary cream of tartar. A salt analogous to Rochelle salt also exists, having ammonium in place of sodium.

The tartrates of *calcium, barium, strontium, magnesium*, and of most of the heavy metals, are insoluble, or nearly so, in water.

Potassio-antimonious Tartrate, or *Tartar emetic*, is easily made by boiling antimony trioxide in solution of cream of tartar: it is deposited from a hot and concentrated solution in rhombic octohedrons, which dissolve without decomposition in 15 parts of cold and 3 of boiling water, and have an acrid extremely disagreeable metallic taste. The solution is decomposed by both acids and alkalis: the former throws down a mixture of cream of tartar and antimony trioxide, and the latter the trioxide, which is again dissolved by great excess of the reagent. Sulphuretted hydrogen separates all the antimony in the state of trisulphide. The dry salt heated on charcoal before the blowpipe, yields a globule of metallic antimony. The crystals contain $2C_4H_4K(SbO)O_6+aq.$, the group SbO acting as a univalent radicle, and replacing one atom of hydrogen. When dried at 100°, they give off their water of crystallisation, and at 200° an additional molecule of water, leaving the compound, $C_4H_2K(SbO)O_5$, which has the constitution of a salt, not of tartaric, but of tartrelic acid, $C_4H_4O_5$. Nevertheless, when dissolved in water, the crystals again take up the elements of water, and reproduce the original salt.

An analogous compound, containing arsenic in place of antimony, has been obtained. It has the same crystalline form as tartar emetic.

A solution of tartaric acid dissolves ferric hydrate in large quantity, forming a brown liquid, which has an acid reaction, and dries up by gentle heat to a brown, transparent, glassy substance, destitute of all traces of crystallisation. It is very soluble in water, and the solution is not precipitated by alkalis, either fixed or volatile. Indeed, tartaric acid, added in sufficient quantity to a solution of ferric oxide, or alumina, entirely prevents the precipitation of the bases by excess of ammonia. Tartrate and ammoniacal tartrate of iron are used in medicine, these compounds having a less disagreeable taste than most of the iron preparations.

Solutions of tartaric acid give with lime and baryta-water, and with lead acetate, white precipitates, which dissolve in excess of the acid; with neutral calcium and barium salts no change is produced. Silver nitrate produces in neutral tartrates a white precipitate of silver tartrate, which dissolves in ammonia. On gently heating the solution, a bright metallic deposit of silver is formed. The reaction of tartaric acid with solutions of potassium salts has been already noticed.

Tartaric Ethers.—1. Tartaric acid forms, with monatomic alcohol-radicles, acid and neutral ethers, in which one or both of the atoms of *basic* hydrogen in its molecule is replaced by an alcohol-radicle. These compounds may be formulated as follows:

$$(C_2H_2)\left\{\begin{matrix}(OH)_2\\(CO_2H)_2\end{matrix}\right. \qquad (C_2H_2)\left\{\begin{matrix}(OH)_2\\CO_2H\\CO_2C_2H_5\end{matrix}\right. \qquad (C_2H_2)\left\{\begin{matrix}(OH)_2\\(CO_2C_2H_5)_2\end{matrix}\right.$$

Tartaric acid. Acid ethyl tartrate. Neutral ethyl tartrate.

The acid ethers are monobasic acids, formed by the direct action of tartaric acid on the respective alcohols; the neutral ethers are formed by passing hydrochloric acid gas into a solution of tartaric acid in an alcohol. Further, by treating these neutral ethers with chlorides of acid radicles, other neutral ethers are formed, in which one or more of the alcoholic hydrogen-atoms are replaced by acid radicles.* In this manner are formed such compounds as the following:

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* Perkin, Chem. Soc. Journ. [2], v. 139.

$$(C_2H_2)\left\{\begin{matrix}OH\\ OC_2H_3O\\ (CO_2C_2H_5)_2\end{matrix}\right.$$

Ethyl aceto-tartrate.

$$(C_2H_2)\left\{\begin{matrix}OC_2H_3O\\ OC_7H_5O\\ (CO_2C_2H_5)_2\end{matrix}\right.$$

Ethyl aceto-benzo-tartrate.

$$\begin{matrix}(C_2H_2)\\ (C_2H_2)\end{matrix}\left\{\begin{matrix}(OH\\ (O_2C_4H_4O_2)\\ (CO_2C_2H_5)_4\end{matrix}\right.$$

Ethyl-succino-tartrate.

The alcoholic hydrogen in these neutral ethers may be replaced by potassium and sodium.

2. There are also *bibasic tartaric ethers* formed by replacing the alcoholic hydrogen of tartaric acid with acid radicles; *e.g.*,

$$(C_2H_2)\left\{\begin{matrix}OH\\ OC_7H_5O\\ (CO_2H)_2\end{matrix}\right.$$

Benzotartaric acid.

$$(C_2H_2)\left\{\begin{matrix}(OC_2H_3O)_2\\ (CO_2H)_2\end{matrix}\right.$$

Diacetotartaric acid.

$$(C_2H_2)\left\{\begin{matrix}(ONO_2)_2\\ (CO_2H)_2\end{matrix}\right.$$

Dinitrotartaric acid.

3. Lastly, tartaric acid forms ethers with glycol, glycerin, mannite, glucose, and other polyatomic alcohols.

Dinitrotartaric acid, $C_2H_2(O.NO_2)_2{<}\begin{matrix}CO_2H\\ CO_2H\end{matrix}$, in which both the alcoholic hydrogen-atoms of tartaric acid are replaced by NO_2, is formed by dissolving finely pulverised tartaric acid in strong nitric acid, and adding sulphuric acid: it then separates as a jelly, which dries up to a white shining mass. It is soluble in water, and the solution when heated yields tartronic acid (p. 358).

Tartaric Anhydrides.—When crystallised tartaric acid is exposed to a temperature of about 204°, it melts, loses water, and yields in succession three different anhydrides, viz.:

Ditartaric or Tartralic acid, . $C_8H_{16}O_{11} = 2C_4H_6O_6 - H_2O$
Tartrelic acid, ... $\left.\begin{matrix}\\ \\ \end{matrix}\right\}$
Insoluble tartaric anhydride, . $\left.\begin{matrix}\\ \\ \end{matrix}\right\}$ $C_4H_4O_5 = C_4H_6O_6 - H_2O$

The first two are soluble in water, and form salts which have properties completely different from those of ordinary tartaric acid. The third is a white insoluble powder. All three, in contact with water, slowly pass into ordinary tartaric acid.

Tartaric acid, subjected to destructive distillation, is resolved into carbon dioxide and pyrotartaric acid, $C_3H_6O_4$.

When tartaric acid is heated to 204·5°, with excess of potassium hydroxide, it is resolved, without charring or secondary decomposition, into oxalic and acetic acids, which remain in union with the base, and undergo decomposition at a much higher temperature:

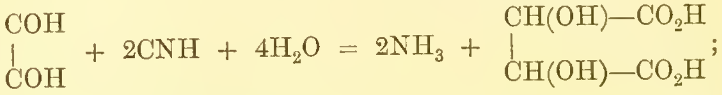
$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} + 2KHO = \underset{\text{Acid potassium oxalate.}}{C_2KHO_4} + \underset{\text{Potassium acetate.}}{C_2H_3KO_2} + 2H_2O.$$

2. LEVOTARTARIC ACID.—This acid resembles dextrotartaric acid in every respect, except that it turns the plane of polarisation to the

left, and that its salts, as well as the acid itself, though isomorphous with the corresponding dextro-tartrates, contain oppositely situated hemihedral faces (see below).

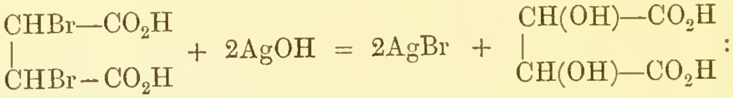
3. Paratartaric or Racemic Acid.—This acid occurs, together with ordinary tartaric acid, in the grapes cultivated in certain districts of the Upper Rhine and in the Vosges. To separate it, the mother liquor of the argol, obtained from these grapes, is boiled with chalk, the calcium salt which separates is decomposed by sulphuric acid, and the filtrate is evaporated to the crystallising point. The crystals of racemic acid being efflorescent, are easily separated by mechanical means from the shining crystals of ordinary tartaric acid.

Racemic acid may be formed artificially by oxidising mannite, dulcite, or mucic acid with nitric acid, and synthetically by boiling glyoxal with hydrocyanic acid and a small quantity of hydrochloric acid:



$$\begin{array}{l}COH\\ |\\ COH\end{array} + 2CNH + 4H_2O = 2NH_3 + \begin{array}{l}CH(OH)—CO_2H\\ |\\ CH(OH)—CO_2H\end{array};$$

further, together with inactive tartaric acid, by boiling dibromosuccinic acid with silver oxide and water:



$$\begin{array}{l}CHBr—CO_2H\\ |\\ CHBr-CO_2H\end{array} + 2AgOH = 2AgBr + \begin{array}{l}CH(OH)—CO_2H\\ |\\ CH(OH)—CO_2H\end{array}:$$

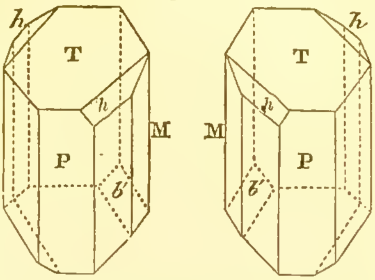
most readily, however, by heating ordinary tartaric acid with about one-tenth of its weight of water to 170°–180° in sealed vessels, the dextrotartaric acid being thereby completely converted into inactive tartaric and racemic acids, which may be separated by crystallisation, the racemic acid being much the less soluble of the two.

The conversion of tartaric acid into racemic acid was originally effected by Pasteur, by heating ethyl tartrate or cinchonine tartrate to about 170°. On repeatedly boiling the product with water, and mixing the cooled solution with excess of calcium chloride, a considerable precipitate of calcium racemate is obtained.

Racemic acid crystallises with 1 molecule of water in rhombic prisms, which give off their water at 100°. It is somewhat less soluble in water than ordinary tartaric acid, and has no action on polarised light. It is in fact a compound of dextro- and levotartaric acids in equal quantities, and may be resolved into those acids through the medium of some of its double salts.

When racemic acid is saturated with potash or soda, or any other single base, a salt is obtained, all the crystals of which are identical in form and in physical properties; but by saturating racemic acid with two bases, as with soda and ammonia, or by mixing the racemates of sodium and of ammonium in equivalent proportions, and evaporating the solution, crystals of a double salt, $C_4H_4O_6Na(NH)_4$, are obtained, analogous to Rochelle salt, the form of which is shown in figure 16. It is a right rectangular prism, P, M, T, having its lateral edges replaced by the faces *b′*, and the intersection of these latter faces with the face T replaced by a face *h*. If the crystal were holohedral, there would be eight of these *h* faces, four above and four below; but, as the figures show, there are but four of them, placed alternately. Moreover, these hemihedral faces occupy in different crystals of the salt, not in similar but opposite or symmetrical positions, the one kind of crystal being as it were the reflected image of the other.

Fig. 16.



Further, by carefully picking out these two kinds of crystals and dissolving them separately in water, solutions are obtained, which, at the same degree of concentration, exert equal and opposite actions upon polarised light, the one deflecting the plane of polarisation to the right, the other by an equal amount to the left. Moreover, the solutions of the right- and left-handed crystals, when evaporated, yield crystals, each of its own kind only; and by mixing the solutions of these crystals with calcium chloride, calcium salts are obtained which, when decomposed by sulphuric acid, yield acids agreeing with each other in composition and in every other respect, excepting that their crystalline forms exhibit opposite hemihedral modifications, and their solutions, when reduced to the same degree of concentration, exert equal and opposite effects on polarised light. One of these acids is in fact dextrotartaric, the other levotartaric acid. A mixture of equal parts of these two acids has no longer the slightest effect on polarised light, and is in every respect identical with racemic acid.

4. Inactive Tartaric Acid or Mesotartaric Acid, is formed by oxidising sorbin (p. 195) with nitric acid; also, together with racemic acid, from dibromosuccinic acid, and from glyoxal (p. 256); but it is most easily prepared by heating ordinary tartaric acid with a little water to 165° for two days. It is separated from unaltered tartaric acid, and from simultaneously formed racemic acid, by converting it into the acid potassium salt, which is very soluble in water.

Inactive tartaric acid is much more soluble in water than ordinary tartaric or racemic acid (10 parts of it dissolve in 8 parts of water at 15°). It does not deflect the plane of polarisation, but differs from racemic acid in not being resolvable into the two active acids. When heated to 170°, however, it is converted into dextrotartaric acid.

Homotartaric Acid, $C_5H_8O_6 = C_6H_4(OH)_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$, of which very little is known, is formed from dibromopyrotartaric acid.

Rhodizonic Acid, $C_5H_4O_6$.—When potassium is heated in a stream of dry carbon monoxide, the latter is absorbed in large quantity, and a black porous substance generated, which, according to Brodie, contains COK_3. Brought in contact with water it decomposes with great violence, and even the dry substance occasionally explodes; when anhydrous alcohol is poured upon it, a great elevation of temperature ensues, but the decomposition is far less violent than with water. The product of this reaction is potassium rhodizonate, which remains as a red powder, insoluble in alcohol, but soluble in water with a deep red colour. This salt probably contains $C_5H_2K_2O_6$.

When solution of potassium rhodizonate is boiled, it becomes orange-yellow from decomposition of the acid, and is then found to contain free potash, and a salt of Croconic acid, $C_5H_2O_5$. This acid can be isolated; it is yellow, easily crystallisable, soluble both in water and alcohol. It is likewise bibasic.

Citric Acid, $C_6H_8O_7 = C_3H_4(OH)_2(CO_2H)_3$.—This acid is obtained in large quantities from the juice of lemons; it is found in many other fruits, as in gooseberries, currants, &c., in conjunction with malic acid. To prepare it, the juice is allowed to ferment a short time, in order that mucilage and other impurities may separate and subside; the clear liquor is then carefully saturated with chalk, whereby insoluble calcium citrate is produced. This is thoroughly washed, decomposed by the proper quantity of sulphuric acid diluted with water, and the filtered solution is evaporated to a small bulk, and left to crystallise. The product is drained from the mother-liquor, redissolved, digested with animal charcoal, and again concentrated to the crystallising point. The acid has not yet been obtained by any synthetical process.

Citric acid crystallises in two different forms. The crystals which separate by spontaneous evaporation from a cold saturated solution, are trimetric prisms, containing $C_6H_8O_7.H_2O$, whereas those which are deposited from a hot solution have a different form, and contain $2C_6H_8O_7.H_2O$.—Citric acid has a pure and agreeable acid taste, and dissolves, with great ease, in both hot and cold water; the solution strongly reddens litmus, and when long kept, is subject to spontaneous change. Citric acid, when brought in contact with putrid flesh as a ferment, yields butyric acid and small quantities of succinic acid. It is entirely decomposed when heated with sulphuric and nitric acids: the latter converts it into oxalic acid. Caustic potash, at a high temperature, resolves it into acetic and oxalic acids. The alkaline citrates, treated with chlorine, yield chloroform, together with other products.

Citric acid is tetratomic and tribasic. With *potassium* it forms a neutral salt containing $C_6H_5K_3O_7$, and two acid salts containing respectively $C_6H_6K_2O_7$ and $C_6H_7KO_7$; and similar salts with the other alkali-metals. With dyad metals it chiefly forms salts in which two or three hydrogen-atoms in the molecule $C_6H_8O_7$, are replaced by metals; with *calcium*, for example, it forms the salts

$C_6H_6CaO_7 + H_2O$ and $(C_6H_5O_7)_2Ca_3 + H_2O$. With *lead* it forms two salts similar in constitution to the calcium salts, and likewise a tetraplumbic salt containing $(C_6H_5O_7)_2Pb_3.PbH_2O_2$.

The citrates of the *alkali-metals* are soluble, and crystallise with greater or less facility; those of *barium, strontium, calcium, lead,* and *silver* are insoluble.

Citric acid resembles tartaric acid in its relations to ferric oxide, preventing the precipitation of that substance by excess of ammonia. The citrate obtained by dissolving hydrated ferric oxide in solution of citric acid, dries up to a pale-brown, transparent, amorphous mass, which is not very soluble in water; an addition of ammonia increases the solubility. Citrate and ammonio-citrate of iron are used as medicinal preparations.

Citric acid is sometimes adulterated with tartaric acid: the fraud is easily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of potassium acetate. If tartaric acid be present, a white crystalline precipitate of cream of tartar will be produced on agitation. Citric acid is further distinguished from tartaric acid by the characters of its calcium salt. An aqueous solution of citric acid is not precipitated by lime-water in the cold, but on boiling a precipitate is formed, consisting of tricalcic citrate, insoluble in potash-ley. Calcium tartrate, on the other hand, dissolves in alkalis, and is precipitated therefrom as a jelly on boiling.

Citric acid forms ethers in which 1, 2, or 3 hydrogen-atoms are replaced by methyl and other monad alcohol-radicles. The neutral ethers are formed by passing gaseous hydrogen chloride into an alcoholic solution of citric acid. The *trimethylic ether*, $C_3H_4(OH)(CO_2.CH_3)$, is crystalline; the *triethylic ether* boils, with partial decomposition, at about 280°.

By treating these neutral ethers with acetyl chloride, the alcoholic hydrogen may also be replaced, and triethylic acetocitrate, $C_3H_4(O.C_2H_3O)(CO_2C_2H_5)_3$, produced, which boils at 288°. By treating the same ethers with nitric acid, the alcoholic hydrogen may be replaced by NO_2.

Pentatomic Acids.

Of these only one is known, viz., the bibasic acid,

Aposorbic acid, $C_5H_8O_7 = C_3H_3(OH)_3<\begin{matrix}CO_2H\\CO_2H\end{matrix}$, which may be regarded as a trioxypyrotartaric acid. It is produced by oxidising sorbin with nitric acid, and crystallises in small laminæ, easily soluble in water, and melting with decomposition at about 110°.

Hexatomic Acids.

Gluconic Acid, $C_6H_{12}O_7 = C_5H_6(OH)_5.CO_2H$, is obtained by oxidising grape-sugar with chlorine-water and removing the chlorine-with silver oxide. It is a non-crystallisable syrup, easily soluble in water, and nearly insoluble in alcohol. It is monobasic. Its calcium and barium salts and the ethylic ether crystallise well; the formula of the calcium salt is $(C_6H_{11}O_7)_2Ca + 2H_2O$.

Mannitic Acid, $C_6H_{12}O_7 = C_5H_6(OH)_5.CO_2H$, is produced by oxidation of mannite, $C_6H_{14}O_6$, under the influence of platinum black. It is a gummy mass, soluble in water and in alcohol, insoluble in ether. According to its mode of formation it might be expected to be monobasic:

$$\begin{array}{ll} \text{Mannite,} & CH_2OH—(CHOH)_4—CH_2OH \\ \text{Mannitic acid,} & CH_2OH—(CHOH)_4—COOH\,; \end{array}$$

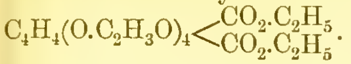
but from the observations of Gorup-Besanez, who discovered it, it appears to be bibasic, its potassium salt containing $C_6H_{10}K_2O_7$, and the calcium salt, $C_6H_{10}CaO_7$.

Saccharic Acid, $C_6H_{10}O_8 = (C_4H_4)\left\{\begin{matrix}(OH)_4\\(CO_2H)_2\end{matrix}\right. = CO.OH—(CHOH)_4—CO.OH$.—This acid is produced by the action of dilute nitric acid on cane sugar, glucose, milk-sugar, and mannite, and is often formed in the preparation of oxalic acid, being, from its superior solubility, found in the mother-liquor from which the oxalic acid has crystallised. It may be made by heating together 1 part of sugar, 2 parts of nitric acid, and 10 parts of water. When the reaction seems terminated, the acid liquid is diluted and neutralised with chalk; the filtered liquid is mixed with lead acetate; and the insoluble lead saccharate is washed, and decomposed by sulphuretted hydrogen. The acid slowly crystallises from a solution of syrupy consistence in long colourless needles; it has a sour taste, and forms soluble salts with lime and baryta. When mixed with silver nitrate it gives no precipitate, but, on the addition of ammonia, a white insoluble substance separates, which, on gently warming the whole, is reduced to metallic silver, the vessel being lined with a smooth and brilliant coating of the metal. Nitric acid converts saccharic into oxalic and dextrotartaric acids.

There are two *potassium saccharates*, containing $C_6H_9KO_8$ and $C_6H_8K_2O_8$; the *silver-salt* contains $C_6H_8Ag_2O_8$; the *barium, magnesium, zinc,* and *cadmium salts* have the composition $C_6H_8M''O_8$; and there are two *ethylic ethers*, containing $C_6H_9(C_2H_5)O_8$ and $C_6H_8(C_2H_5)_2O_8$. In these compounds saccharic acid appears to be bibasic, as might be expected from its constitution, and mode of formation; the composition of the lead-salts, however, seems to show that it is sexbasic as well as hexatomic, for Heintz has obtained a lead-salt containing $C_6H_4Pb_3O_8$; but the composition of the lead saccharates varies considerably according to the manner in which they are prepared.

Diethylic Saccharate, $C_4H_4(OH)_4{<}\begin{matrix}CO_2.C_2H_5\\CO_2.CO_2H_5\end{matrix}$, is crystalline, and easily soluble in water. Ammonia converts it into the amide

$C_4H_4(OH)_4(CO.NH_2)_2$, which is a white powder. The ether, treated with acetyl chloride, yields the tetracetylic compound



$$C_4H_4(O.C_2H_3O)_4<\begin{matrix}CO_2.C_2H_5\\CO_2.C_2H_5\end{matrix}.$$

Mucic Acid, $C_6H_{10}O_8 = C_4H_4(OH)_4(CO_2H)_2$, isomeric with saccharic acid, is produced, together with a small quantity of oxalic acid, by the action of rather dilute nitric acid on sugar and gum. It may be easily prepared by heating together in a flask or retort, 1 part of milk-sugar or gum, 4 parts of nitric acid, and 1 part of water; the mucic acid is afterwards collected upon a filter, washed and dried. It has a slightly sour taste, and reddens vegetable colours. It requires for solution 66 parts of boiling water. By prolonged boiling with water, it is converted into the isomeric paramucic acid. By boiling with nitric acid it is resolved into oxalic and racemic acids. It is decomposed by heat, yielding, among other products, pyromucic acid, $C_5H_4O_3$:

$$C_6H_{10}O_8 = C_5H_4O_3 + CO_2 + 3H_2O.$$

Mucic acid is bibasic, yielding for the most part neutral salts containing $C_6H_8M_2O_8$ and $C_6H_8M''O_8$; with the alkali-metals it also forms acid salts, such as $C_6H_9KO_8$.

The neutral potassium and ammonium salts crystallise well, and are but slightly soluble in cold water; the acid salts are easily soluble. The neutral ammonium salt is resolved by heat into ammonia, water, and pyrrol, C_4H_5N.

Diethylic Mucate, $C_4H_4(OH)_4(CO_2.C_2H_5)_2$, obtained by heating mucic acid with alcohol and sulphuric acid, is crystalline, soluble in hot water, melts at 158°, and is converted by acetyl chloride into the tetracetyl compound, $C_4H_4(O.C_2H_3O)_4(CO_2.C_2H_5)_2$, which melts at 177°.

Deoxalic or **Racemo-carbonic Acid**, $C_6H_8O_9$, probably $= C_3H_2(OH)_3(CO_2H)_3$, is produced by the action of sodium amalgam on ethylic oxalate:

$$3C_2H_2O_4 + 4H_2 = 3H_2O + C_6H_8O_9.$$

Deoxalic acid is not known in the free state, being resolved, on evaporation of its aqueous solution, into racemic and glyoxylic acids:

$$C_6H_8O_9 = C_4H_6O_6 + C_2H_2O_3.$$

The acid is essentially tribasic, its ammonium salt having the composition $C_6H_5(NH_4)_3O_9 + H_2O$; but it also forms salts in which 4 atoms of hydrogen (one alcoholic) are replaced by metal, the silver salt being $C_6H_4Ag_4O_9 + H_2O$, and the barium salt $C_6H_4Ba_2O_9 + 3H_2O$. By the action of acetic acid on its potassium salt it is resolved into acetic acid and Löwig's deoxalic acid, $C_5H_6O_8$:

$$2C_6H_8O_9 = C_2H_4O_2 + 2C_5H_6O_8.$$

This last acid, $C_2H(OH)_2.(CO_2H)_3$, forms large colourless crystals, easily soluble in water and in alcohol. It is tribasic. Heated with water to 100°, it is resolved into racemic acid and carbon dioxide :

$$C_5H_6O_8 = C_4H_6O_6 + CO_2 .$$

Pyromucic Acid and its Derivatives.

Pyromucic Acid, $C_5H_4O_3 = C_4H_3O.COOH$, is produced by the dry distillation of mucic acid, or more advantageously by boiling furfurol with water and recently precipitated silver oxide; the silver is precipitated by hydrochloric acid, the filtrate evaporated, and the pyromucic acid purified by crystallisation from dilute alcohol.

Pyromucic acid crystallises in colourless laminæ or needles, easily soluble in water, especially if hot, moderately soluble in alcohol. It melts at 134°, and sublimes at 100°. It is monobasic. The *silver salt*, $C_5H_3O_3Ag$, crystallises in laminæ; the *barium salt*, $(C_5H_3O_3)_2Ba$, forms crystals easily soluble in water. The *ethylic ether*, $C_5H_3O_3.C_2H_5$, obtained by distilling the acid with hydrochloric acid and alcohol, is a crystalline mass, melting at 34°, and boiling at 208°–210°. The *chloride*, $C_4H_3O.COCl$, produced by distilling pyromucic acid with phosphorus pentachloride, boils at 170°, and is converted by ammonia into the *amide*, $C_4H_3O.CONH_2$, a crystalline substance, soluble in water, and melting at 130°.

Barium pyromucate, distilled with soda-lime, yields tetraphenol, C_4H_4O, or $C_4H_3O.OH$ (4-carbon phenol), as a colourless liquid, boiling at 32°.

Isopyromucic acid, $C_5H_4O_3$, is produced, together with pyromucic acid, by the dry distillation of mucic acid, and may be separated from the latter by solution in a small quantity of cold water. It sublimes below 100° in white laminæ, which turn yellow on exposure to the air, melt at 82°, dissolve very easily in water, alcohol, and ether.

Carbopyrollamide, $C_5H_6N_2O = C_4H_2{<}\genfrac{}{}{0pt}{}{CO.NH_2}{NH_2}$, produced by dry distillation of ammonium pyromucate, forms white shining laminæ, easily soluble in alcohol and in ether. It melts at 173°, and does not resolidify till cooled to 133°. By boiling with water it is resolved into ammonia and carbopyrrolic acid :

$$C_5H_6N_2O + H_2O = NH_3 + C_5H_5NO_2 .$$

Carbopyrrolic acid, $C_4H_2{<}\genfrac{}{}{0pt}{}{CO_2H}{NH_2}$, crystallises in small prisms, sublimes at about 190°, and is decomposed by sudden heating into carbon dioxide and pyrrol :

$$C_5H_5NO_2 = CO_2 + C_4H_5N .$$

Barium carbopyrrolate crystallises in large laminæ.

Pyrrol, C_3H_5N, is a weak base occurring in coal-tar oil and in bone-oil, and producible by distillation of ammonium pyromucate and of carbopyrrolic acid. It may be prepared from bone-oil by dissolving out the basic constituents with sulphuric acid, and submitting the acid solution to prolonged boiling, whereby the stronger bases are retained, while the pyrrol distils over. The distillate is heated with solid potassium hydroxide, when the pyrrol combines slowly with the alkali, admixed impurities being volatilised. On dissolving the potassium-compound in water, the pyrrol separates on the surface as an oily liquid. Pyrrol is colourless, insoluble in water and alkalis, slowly soluble in acids : it has an ethereal odour resembling that of chloroform, a specific gravity $= 1{\cdot}077$, and boils at 133°. It is easily recognised by the purple colour which it imparts to fir-wood moistened with hydrochloric acid.

By heating an acid solution of pyrrol, a red, flaky substance, *pyrrol-red*, is produced, containing $C_{12}H_{14}N_2O$, the formation of which is represented by the following equation :

$$3C_4H_5N + H_2O = C_{12}H_{14}N_2O + NH_3.$$

Furfurol, $C_5H_4O_2 = C_4H_3O.COH$.—This compound, which is the aldehyde of pyromucic acid, is formed in the dry distillation of sugar, and by distilling bran with dilute sulphuric acid or zinc chloride. To prepare it, 1 part of bran is mixed with 1 part of sulphuric acid diluted with 3 parts of water, and the distillate is saturated with sodium carbonate, mixed with common salt, and distilled. On adding common salt to this second distillate, the furfurol separates from the watery liquid in the form of a heavy oil.

Furfurol is a colourless liquid, having an agreeable odour, somewhat like that of oil of cassia. It boils at 162°, has a specific gravity of 1·164, vapour density $= 3{\cdot}493$ (referred to air), dissolves in 12 parts of water at 13°, very easily in alcohol.

Furfurol, like other aldehydes, unites with acid sodium sulphite, forming a crystalline compound, $C_5H_4O_2.SO_3NaH$, sparingly soluble in alcohol, and is converted by sodium amalgam into an alcohol, viz., furfuryl alcohol, $C_5H_6O_2$. By oxidation with silver oxide, it is converted into pyromucic acid, and by nitric acid into oxalic acid. With ammonia it forms furfuramide: $3C_5H_4O_2 + 2NH_3 = (C_5H_4O)_3N_2 + 3H_2O$.

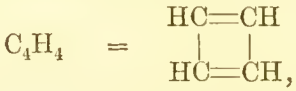
Furfuryl Alcohol, $C_5H_5O.OH$, produced by the action of sodium amalgam on furfurol or on pyromucic acid, is a thick oil, insoluble in water, and decomposing when distilled.

Furfuramide, $(C_5H_4O)_3N_2$, is formed when furfurol is left for a few hours in contact with aqueous ammonia, and separates in white crystals, insoluble in water, but easily soluble in alcohol and ether. By boiling with water or acids it is resolved into ammonia and furfurol. By heating to 120°, or by boiling with dilute aqueous potash, it is converted into the isomeric compound furfurine (discovered by Fownes), which is a crystalline base, melting at 100°, and forming crystallisable very bitter salts, containing 1 eq. of acid.

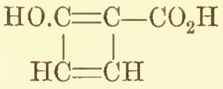
Furfurine is sparingly soluble in cold water, dissolves in about 135 parts of boiling water, easily in alcohol and ether, forming solutions which have a strong alkaline reaction.

Fucusol.—By treating several varieties of fucus with sulphuric acid in exactly the same manner as in the preparation of furfurol, Dr. Stenhouse has obtained a series of substances, which he designates by the terms *fucusol*, *fucusamide*, and *fucusine*. They have exactly the same composition as the corresponding terms in the furfurol series, and also most of their properties, but differ in some respects.

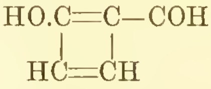
The constitution of the compounds just described is not very well understood: they cannot be regarded as derivatives either of methane or of benzene, in other words, as belonging either to the fatty or to the aromatic group, but they may be represented, provisionally at least, by constitutional formulæ derived from that of a hypothetical hydrocarbon called tetrene:



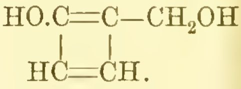
intermediate in composition between acetylene and benzene; thus:



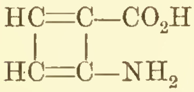
Pyromucic acid.



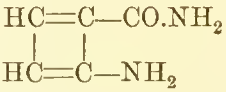
Furfurol.



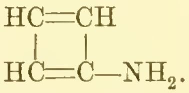
Furfuryl alcohol.



Carbopyrrolic acid.



Carbopyrrolamide.



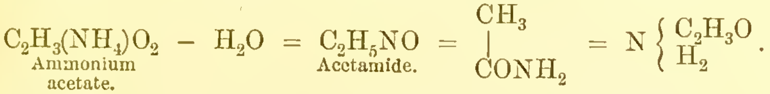
Pyrrol.

AMIDES.

We have had frequent occasion to speak of these compounds, as derived from ammonium-salts by abstraction of water, or from acids by substitution of amidogen, NH_2, for hydroxyl, OH, or from one or more molecules of ammonia by substitution of acid-radicles for hydrogen. They are divided (like amines) into monamides, diamides, and triamides, each of which groups is further subdivided into primary, secondary, and tertiary amides, according as one-third, two-thirds, or the whole of the hydrogen is replaced by acid-radicles. If the hydrogen is replaced partly by acid-radicles, and partly by alcohol-radicles, the compound is called an alkalamide; for example, ethylacetamide, $NH(C_2H_5)(C_2H_3O)$; ethyldiacetamide, $N(C_2H_5)(C_2H_3O)_2$.

AMIDES DERIVED FROM MONATOMIC ACIDS.

A monatomic acid yields but one primary amide, which may be formed: 1. From its ammonium-salt by direct abstraction of a molecule of water, under the influence of heat; thus:



$$\underset{\substack{\text{Ammonium}\\\text{acetate.}}}{C_2H_3(NH_4)O_2} - H_2O = \underset{\text{Acetamide.}}{C_2H_5NO} = \begin{array}{c} CH_3 \\ | \\ CONH_2 \end{array} = N\left\{\begin{array}{l} C_2H_3O \\ H_2 \end{array}\right. .$$

This method is especially adapted to the preparation of volatile amides.

2. By the action of ammonia on acid chlorides or anhydrides:

$$\underset{\text{Acetic chloride.}}{C_2H_3O.Cl} + 2NH_3 = NH_4Cl + \underset{\text{Acetamide.}}{C_2H_3O.NH_2}$$

$$\underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} + 2NH_3 = NH_4.O.C_2H_3O + C_2H_3O.NH_2 .$$

This method is especially adapted to the preparation of amides which are insoluble in water.

3. By the action of ammonia on compound ethers:

$$\underset{\text{Ethyl acetate.}}{C_2H_3O.O.C_2H_5} + NH_3 = C_2H_5.OH + C_2H_3O.NH_2 .$$

This reaction often takes place at ordinary temperatures, but is for the most part best effected by heating the two bodies together in alcoholic solution.

Secondary monamides are those in which two atoms of hydrogen in a molecule of ammonia are replaced by two univalent or one bivalent acid-radicle, or by one acid-radicle and one alcohol-radicle. Those containing only univalent radicles are formed by the action of dry hydrochloric acid gas on primary monamides at a high temperature; *e.g.*, diacetamide from acetamide:

$$2NH_2(C_2H_3O) + HCl = NH_4Cl + NH(C_2H_3O)_2 .$$

Those containing bivalent acid-radicles are called imides; *e.g.*, succinimide, $NH(C_4H_4O_2)$. They are derived from bibasic acids, and will be noticed further on.

Secondary monamides (alkalamides) containing an acid-radicle and an alcohol-radicle, are formed by processes similar to those above given for the formation of the primary monamides, substituting amines for ammonia; thus:

$$\underset{\substack{\text{Acetic}\\\text{chloride.}}}{C_2H_3OCl} + \underset{\text{Ethylamine.}}{NH_2(C_2H_5)} = HCl + \underset{\text{Ethyl-acetamide.}}{NH(C_2H_5)(C_2H_3O)}$$

$$\underset{\text{Ethyl acetate.}}{C_2H_3O(OC_2H_5)} + \underset{\text{Ethylamine.}}{NH_2(C_2H_5)} = \underset{\text{Alcohol.}}{HOC_2H_5} + \underset{\text{Ethyl-acetamide.}}{NH(C_2H_5)(C_2H_3O)}$$

Tertiary monamides are those in which the whole of the hydrogen in one molecule of ammonia is replaced by acid-radicles or by acid- and alcohol-radicles. Those of the latter kind, called tertiary alkalamides, are produced by the action of acid chlorides on secondary alkalamides:

$$\underset{\text{Ethyl-acetamide.}}{NH(C_2H_5)(C_2H_3O)} + \underset{\text{Acetyl chloride.}}{C_2H_3O.Cl} = HCl + \underset{\text{Ethyl-diacetamide.}}{N(C_2H_5)(C_2H_3O)_2};$$

or by the action of monatomic acid oxides on cyanic ethers; *e.g.*:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl cyanate.}}{N(CO)(C_2H_5)} = CO_2 + \underset{\text{Ethyl-diacetamide.}}{N(C_2H_5)(C_2H_3O)_2}.$$

Monamides are for the most part crystalline bodies soluble in alcohol and ether. The lower members of the group are likewise soluble in water, and distil without decomposition. As they contain both a basic group (NH_2), and an acid group, they are capable of acting both as bases and as acids, combining, on the one hand, with acids to form saline compounds, such as $C_2H_3O.NH_2.NO_2H$, which, however, are not very stable; and, on the other hand, forming salts by substitution of a metal for one atom of hydrogen; thus *silver-acetamide*, $C_2H_3O.NHAg$, is obtained in crystalline scales, by saturating an aqueous solution of acetamide with silver oxide.

Amides are less stable than amines, the combination of the amidogen-group with acid radicles (C_2H_3O, for example), being weaker than the combination of the same group with hydrocarbons, as in the amines. Consequently they are more easily decomposed than amines, their decomposition being effected by heating with water, or more readily with alkalis:

$$\underset{\text{Acetamide.}}{C_2H_3O.NH_2} + HOH = NH_3 + \underset{\text{Acetic acid.}}{C_2H_3O.OH}.$$

Primary amides heated with *phosphoric anhydride* or *phosphorus trichloride*, give off 1 mol. water, and are converted into nitrils or alcoholic cyanides; *e.g.*, acetamide into methyl cyanide or acetonitril:

$$CH_3.CO.NH_2 - H_2O = CH_3.CN.$$

When phosphorus pentachloride acts upon an amide, the oxygen-atom of the latter is first replaced by two atoms of chlorine, and the resulting chloride when heated gives up 1 mol. HCl; thus:

$$CH_3.CONH_2 + PCl_5 = PCl_3O + CH_3.CCl_2.NH_2;$$

and

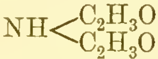
$$CH_3.CCl_2.NH_2 = 2HCl + CH_3.CN.$$

Formamide, $CH_3NO = CHO.NH_2$, the amide of formic acid, is obtained by dry distillation of ammonium formate, or by heating ethyl formate to 100° with alcoholic ammonia. It is a liquid which dissolves easily in water and in alcohol, and boils with partial decomposition, at 192°–195°. When quickly heated, it is resolved into carbon monoxide and ammonia. By dehydration with phosphoric anhydride it is converted into hydrogen cyanide or formonitril, CHN.

Acetamide, $C_2H_5NO = C_2H_3O.NH_2$, may be obtained by either of the general reactions above described; also by distilling a mixture of dry sodium acetate and sal-ammoniac in equal numbers of molecules. It crystallises in long needles, melts at 78°–79°, and boils without decomposition at 222°. It dissolves easily in water and in alcohol, and when heated with acids or alkalis it takes up water and is resolved into acetic acid and ammonia. It unites with acids, forming unstable compounds, *e.g.*, $C_2H_5NO.HCl$, and $C_2H_5NO.NO_3H$. On boiling its aqueous solution with mercuric oxide, the latter is dissolved, and the solution on cooling deposits crystals of *mercuracetamide* $(C_2H_5NO)_2Hg$.

Chloracetamides may be prepared from the three chloracetic acids in the same manner as acetamide from acetic acid. Their melting and boiling points are as follows:

		M. P.	B. P.
Monochloracetamide,	$C_2H_2ClO.NH_2$	116°	224°–225°
Dichloracetamide,	$C_2HCl_2O.NH_2$	96°	233°–234°
Trichloracetamide,	$C_2Cl_3O.NH_2$	136°	238°–239°



Diacetamide, $NH<\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}$, obtained by heating acetamide in a stream of hydrogen chloride, forms crystals easily soluble in water, melts at 59°, and boils at 210°–215°.

Triacetamide, $(C_2H_3O)_3N$, obtained by heating acetonitril to 200° with acetic anhydride, melts at 78°–79°.

Propionamide, $C_3H_5O.NH_2$, is very much like acetamide, melts at 75°–76°, and boils at 210°.

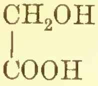
Butyramide, $C_4H_7O.NH_2$, crystallises in laminæ, melts at 115° and boils at 216°.

Isovaleramide, $C_5H_9O.NH_2$, obtained from isovaleric acid, sublimes in laminæ which are soluble in water.

AMIDES DERIVED FROM DIATOMIC AND MONOBASIC ACIDS.

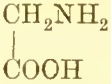
Acids of this group may give rise to two monamides, both formed by substitution of NH_2 for OH, and therefore having the same composition. They are, however, isomeric, not identical, the one formed by replacement of the alcoholic hydroxyl being acid, while the other, formed by replacement of the basic hydroxyl, is neutral. The acid amides thus formed are called amic or amidic acids.

Glycollic acid, for example, yields amidoglycollic or glycollamic acid and glycollamide, both containing $C_2H_5NO_2$:



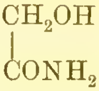
$\begin{array}{l}CH_2OH\\ |\\ COOH\end{array}$

Glycollic acid.



$\begin{array}{l}CH_2NH_2\\ |\\ COOH\end{array}$

Glycollamic acid.

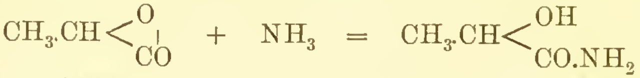


$\begin{array}{l}CH_2OH\\ |\\ CONH_2\end{array}$

Glycollamide.

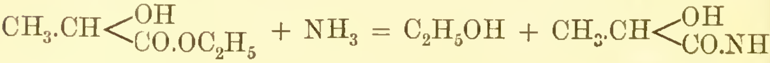
1. Neutral Amides.

These compounds are formed by the action of ammonia in the gaseous state or in alcoholic solution on the corresponding oxides or anhydrides, or on the ethylic ethers of the acids; thus:



$$CH_3.CH{<}\begin{array}{l}O\\ \;|\\ CO\end{array} + NH_3 = CH_3.CH{<}\begin{array}{l}OH\\ CO.NH_2\end{array}$$

Lactide. Lactamide.



$$CH_3.CH{<}\begin{array}{l}OH\\ CO.OC_2H_5\end{array} + NH_3 = C_2H_5OH + CH_3.CH{<}\begin{array}{l}OH\\ CO.NH_2\end{array}$$

Ethyl lactate. Lactamide.

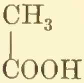
Glycollamide, $C_2H_5NO_2 = CH_2{<}\begin{array}{l}OH\\ CO.NH_2\end{array}$, is formed by heating glycollide, $\begin{array}{l}CH_2\\ |\\ CO\end{array}{>}O$, with dry ammonia, and by heating acid ammonium tartronate (p. 358) to 150°; $C_3H_3(NH_4)O_5 = C_2H_5NO_2 + CO_2 + H_2O$. It crystallises in needles having a sweetish taste, easily soluble in water, sparingly in alcohol, melting at 100°. By boiling with alkalis, it is resolved into glycollic acid and ammonia.

Lactamide, $C_3H_7NO_2 = CH_3.CH{<}\begin{array}{l}OH\\ CO.NH_2\end{array}$, obtained as above mentioned, forms crystals easily soluble in water, melting at 74°, resolved by boiling with alkalis into lactic acid and ammonia.

Lactimide, $C_3H_5NO = CH_3—\overset{\ulcorner\!-CO-\!\urcorner}{CH—NH}$, produced by heating alanine, $CH_3—CH{<}\begin{array}{l}NH_2\\ CO.OH\end{array}$, to 180°–200° in a stream of hydrogen chloride, forms colourless laminæ or needles, easily soluble in water and in alcohol, melting at 275°.

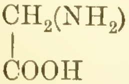
2. Amic or Amidic Acids.

The amic acids of this group are identical with the amidated acids derived from the corresponding monatomic acids, $C_nH_{2n}O_2$, by substitution of amidogen for hydrogen; thus glycollamic acid is identical with amidacetic acid; lactamic with amidopropionic; leucamic with amidocaproic acid; for example:



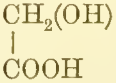
$\begin{array}{l}CH_3\\ |\\ COOH\end{array}$

Acetic acid.



$\begin{array}{l}CH_2(NH_2)\\ |\\ COOH\end{array}$

Amidacetic or Glycollamic acid.



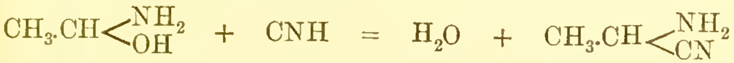
$\begin{array}{l}CH_2(OH)\\ |\\ COOH\end{array}$

Glycollic acid.

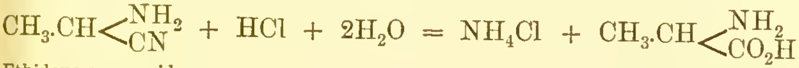
They are formed: 1. By the action of ammonia on the monochloro-, bromo-, or iodo- substitution-products of the fatty acids: *e.g.*,

$$\underset{\text{Chloracetic acid.}}{CH_2Cl.CO_2H} + 2NH_3 = NH_4Cl + \underset{\text{Amidacetic acid.}}{CH_2.NH_2.CO_2H}$$

2. By heating the ammonia-compounds of the aldehydes with hydrocyanic and hydrochloric acid, whereby cyanides are produced in the first instance, and afterwards transformed into amido-acids by the action of the hydrochloric acid:



$$\underset{\text{Aldehyde-ammonia.}}{CH_3.CH{<}\begin{smallmatrix}NH_2\\OH\end{smallmatrix}} + CNH = H_2O + \underset{\text{Ethidene-cyanamide.}}{CH_3.CH{<}\begin{smallmatrix}NH_2\\CN\end{smallmatrix}}$$

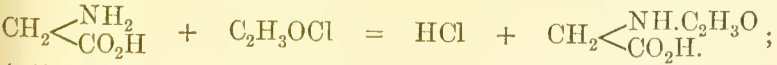


$$\underset{\text{Ethidene-cyanamide.}}{CH_3.CH{<}\begin{smallmatrix}NH_2\\CN\end{smallmatrix}} + HCl + 2H_2O = NH_4Cl + \underset{\text{Lactamic acid.}}{CH_3.CH{<}\begin{smallmatrix}NH_2\\CO_2H\end{smallmatrix}}$$

Several of them occur in the animal organism.

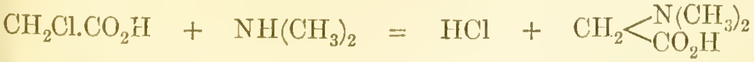
These amic acids are distinguished from the isomeric neutral amides by the more intimate state of combination of their amidogen-group, which cannot be separated by boiling with alkalis. As they contain both a carboxyl-group and an amidogen-group, they possess both acid and basic properties, and form saline compounds both with acids and with bases, the basic character, however, predominating. Hence they are often designated by names ending in *ine*, the ordinary termination for organic bases, glycollamic acid being designated as glycocine, lactamic acid as alanine, leucamic acid as leucine, &c. They are also designated, as a group, by the name Alanines.

The hydrogen of the carboxyl-group in these compounds may be replaced by alcohol-radicles, yielding compound ethers, which, however, are somewhat unstable; that of the amidogen-group may be replaced by alcohol-radicles or by acid-radicles. The acid derivatives are obtained by treating the amido-acids, or their ethers with the haloïd compounds of acid-radicles:



$$\underset{\text{Amidacetic acid.}}{CH_2{<}\begin{smallmatrix}NH_2\\CO_2H\end{smallmatrix}} + \underset{\text{Acetic chloride.}}{C_2H_3OCl} = HCl + \underset{\text{Acetyl-amidacetic acid.}}{CH_2{<}\begin{smallmatrix}NH.C_2H_3O\\CO_2H.\end{smallmatrix}};$$

the alcoholic derivatives by the action of amines on substitution-derivatives of the fatty acids:



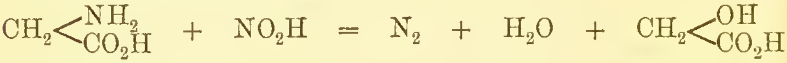
$$\underset{\text{Chloracetic acid.}}{CH_2Cl.CO_2H} + \underset{\text{Dimethylamine.}}{NH(CH_3)_2} = HCl + \underset{\text{Dimethyl-amidacetic acid.}}{CH_2{<}\begin{smallmatrix}N(CH_3)_2\\CO_2H\end{smallmatrix}}$$

The alanines are crystalline bodies, mostly having a sweetish taste, easily soluble in water, insoluble for the most part in alcohol and ether. They have a neutral reaction, and, as already observed, are not decomposed by boiling with alkalis, but when fused with alkaline hydrates, they are decomposed into ammonia and fatty acids. By dry distillation, especially in contact with baryta, they are resolved into amines and carbon dioxide:

$$\mathrm{CH_3.CH}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{CO_2H}} \;=\; \mathrm{CO_2} \;+\; \mathrm{CH_3.CH_2.NH_2}$$

Alanine. Ethylamine.

Nitrous acid converts them into oxyacids:



$$\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{CO_2H}} \;+\; \mathrm{NO_2H} \;=\; \mathrm{N_2} \;+\; \mathrm{H_2O} \;+\; \mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{CO_2H}}$$

Glycocine. Glycollic acid.

Amidacetic Acid, or **Glycocine,** $C_2H_5NO_2 = \mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{CO_2H}}$, also called *amidoglycollic acid, glycollamic acid,* and *glycocoll,* is formed by the action of ammonia on bromacetic or chloracetic acid:

$$C_2H_3ClO_2 + 2NH_3 = NH_4Cl + C_2H_3(NH_2)O_2;$$

also by the action of acids or alkalis upon animal substances, such as glue, hippuric acid, glycollic acid, &c. From hippuric acid it is formed, together with benzoic acid, according to the equation:

$$C_9H_9NO_3 + H_2O = C_2H_5NO_2 + C_7H_6O_2.$$

Glycocine crystallises from water in large hard, transparent, rhombic prisms, having a sweetish taste, soluble in 4 parts of cold water, insoluble in alcohol and ether. It melts at 170°, and decomposes at a higher temperature. By heating with baryta it is resolved into carbon dioxide and methylamine; by treatment with nitrous acid it is converted into glycollic acid. It combines with acids in different proportions. With *sulphuric acid* it forms the compound $(C_2H_5NO_2)_2SO_4H_2$; and on addition of alcohol to a solution of this sulphate, a salt crystallising in rectangular prisms is deposited, containing $3C_2H_5NO_2.SO_4H_2$. It also forms the *hydrochlorides,* $C_2H_5NO_2.HCl$ and $C_2H_5NO_2.2HCl$, the latter of which crystallises in long prisms. The *nitrate,* $C_2H_5NO_2.NO_3H$, forms large prisms.

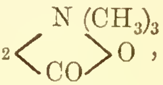
Glycocine also forms saline compounds by substitution of metals for hydrogen; thus it dissolves *cupric oxide,* forming the salt, $(C_2H_4NO_2)_2Cu + H_2O$, which crystallises from the hot solution in dark blue needles. The *silver salt,* $C_2H_4NO_2Ag$, crystallises over sulphuric acid. Glycocine also unites with *metallic salts,* forming crystalline compounds, such as $C_2H_5NO_2.NO_3K$, and $C_2H_5NO_2.NO_3Ag$.

The ethylic ether of glycocine, or *ethyl amidacetate,* $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{CO_2.C_2H_5}}$, is produced by the action of silver oxide on the hydriodide obtained by heating glycocine with ethyl iodide in alcoholic solution. It is resolved by evaporation of its aqueous solution into glycocine and alcohol.

Methyl-glycocine or *Sarcosine*, $C_3H_7NO_2 = CH_2{<}\genfrac{}{}{0pt}{}{NH.CH_3}{CO_2H}$, isomeric with alanine, is formed by digesting ethyl chloracetate with excess of a concentrated aqueous solution of methylamine:

$$CH_2Cl.CO_2.C_2H_5 + CH_3.NH_2 + H_2O$$
$$= HCl + C_2H_5.OH + CH_2{<}\genfrac{}{}{0pt}{}{NH.CH_3}{CO_2H}.$$

The same compound is formed by boiling creatine with baryta-water. The creatine splits into sarcosine and urea, the latter being further decomposed into ammonia and carbonic acid. Sarcosine crystallises in colourless rhombic prisms, easily soluble in water; it is difficultly soluble in alcohol, insoluble in ether, and has no action upon vegetable colours. It combines with acids to form soluble salts, which have an acid reaction. The double salt of sarcosine with platinum tetrachloride crystallises in large yellow octohedrons having the compos tion $2C_3H_7NO_2.2HCl.PtCl_4 + 2$ aq. Sarcosine ignited with soda-lime gives off methylamine.



Trimethyl-glycocine or *Betaine*, $C_5H_{11}NO_2 = CH_2{<}\genfrac{}{}{0pt}{}{N(CH_3)_3}{CO}{>}O$, which exists ready-formed in beet-juice, and is produced by oxidation of choline hydrochloride, and synthetically by heating trimethylamine with monochloracetic acid, has been already described (p. 223).

Ethyl-glycocine, $C_4H_9NO_2 = CH_2{<}\genfrac{}{}{0pt}{}{NH.C_2H_5}{CO_2H}$, obtained by heating chloracetic acid with ethylamine, forms deliquescent laminæ; it unites with acids, bases, and salts.

Diethyl-glycocine, $C_6H_{13}NO_2 = CH_2{<}\genfrac{}{}{0pt}{}{N(C_2H_5)_2}{CO_2H}$, prepared from chloracetic acid and diethylamine, forms deliquescent crystals, and sublimes below 100°.

Acetyl-glycocine or *Aceturic acid*, $CH_2{<}\genfrac{}{}{0pt}{}{NH.C_2H_3O}{CO_2H}$, produced by the action of acetyl chloride on silver-glycocine, or of acetamide on monochloracetic acid, crystallises in small needles, easily soluble in water and in alcohol, and turning brown at 130°; reacts like a monobasic acid.

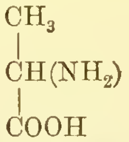
DIGLYCOLLAMIC and TRIGLYCOLLAMIC ACIDS. — Glycocine or glycollamic acid may be regarded as ammonia having one atom of hydrogen replaced by the univalent group $CH_2.CO_2H$, and the similar replacement of 2 and 3 hydrogen-atoms in ammonia may give rise to di- and tri-glycollamic acids:

$NH_2.CH_2.CO_2H$,	Glycollamic acid.
$NH(CH_2.CO_2H)_2$,	Diglycollamic acid.
$N(CH_2.CO_2H)_3$,	Triglycollamic acid.

These three acids are produced simultaneously by boiling monochloracetic acid with strong aqueous ammonia; and on concentrating the resulting solution, filtering from separated sal-ammoniac, boiling the filtrate with lead oxide, and filtering again, the filtrate on cooling deposits the lead salt of triglycollamic acid, while the lead salts of the other two acids remain in solution. To separate the diglycollamic acid, the lead is precipitated by hydrogen sulphide, and the filtered solution is boiled with zinc carbonate, whereupon the sparingly soluble zinc diglycollamate separates out, while the zinc-salt of glycocine remains in solution.

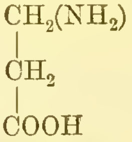
Diglycollamic and triglycollamic acids are crystalline bodies which form salts both with acids and with bases; the former is bibasic, the latter tribasic.

Amidopropionic Acids, $C_3H_7NO_2 = C_3H_5(NH_2)O_2$.—Of these there are two modifications, analogous to the two bromo-, chloro-, and iodo- propionic acids, viz.:



$$\begin{array}{c} CH_3 \\ | \\ CH(NH_2) \\ | \\ COOH \end{array}$$

α-Amidopropionic acid or Alanine.



$$\begin{array}{c} CH_2(NH_2) \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

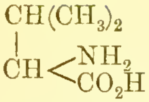
β-Amidopropionic acid.

Alanine is produced by the action of alcoholic ammonia on α-chloro- or α-bromo-propionic acid, or by heating aldehyde-ammonia with hydrocyanic and hydrocloric acids, the reactions being precisely similar to those by which glycocine is obtained from the corresponding derivatives of acetic acid. It crystallises in tufts of hard needles, dissolves in 5 parts of cold water, less easily in alcohol, and is insoluble in ether. When slowly heated it melts and sublimes undecomposed; but when quickly heated, it is resolved into carbon dioxide and ethylamine. Nitrous acid converts it into lactic acid.

Alanine unites with acids, bases, and salts. The *platinochloride*, $2(C_3H_7N_2O.HCl).PtCl_4$, crystallises in large reddish prisms.

β-Amidopropionic acid, $CH_2(NH_2)—CH_2.CO_2H$, prepared by the action of ammonia on β-iodopropionic acid, forms rhombic prisms easily soluble in water, and sublimes with partial decomposition when heated. Its copper compound is much more soluble than that of the α-acid.

α-Amidobutyric Acid, $C_4H_9NO_2 = CH_3.CH_2.CH<{NH_2 \atop CO_2H}$, also called *Propalanine*, is prepared from α-bromobutyric acid. It crystallises in small laminæ or needles, easily soluble in water.

α-Amidisovaleric Acid, $C_5H_{11}NO_2$ =  $\begin{matrix}CH(CH_3)_2\\ | \\ CH<\begin{matrix}NH_2\\CO_2H\end{matrix}\end{matrix}$, occurs in the pancreas of the ox, and is formed artificially by the action of ammonia on bromisovaleric acid. It crystallises in shining prisms, sublimes without previous fusion, dissolves in water and alcohol, but less easily than leucine.

Amidocaproic Acid or **Leucine,** $C_6H_{13}NO_2 = C_5H_{10}<\begin{matrix}NH_2\\CO_2H\end{matrix}$, is formed by the action of ammonia on bromocaproic acid, and by digesting valeral-ammonia with hydrocyanic and hydrochloric acids:

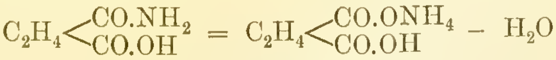
$$C_5H_{10}O.NH_3 + CNH + HCl + H_2O = C_6H_{13}NO_2 + NH_4Cl.$$

Leucine is also formed by the decomposition of animal substances, such as glue, horn, wool, &c., during putrefaction, and by the treatment of these substances with acids or alkalis. It was first discovered in putrid cheese; more recently it has been found in several parts of the animal organism.

Leucine crystallises in white shining scales, which melt at 100°, and may be sublimed without decomposition; it is but little soluble in water, still less in alcohol, insoluble in ether. When heated with caustic baryta, it splits into carbon dioxide and amylamine: $C_6H_{13}NO_2 = C_5H_{13}N + CO_2$. It unites with acids, bases, and salts. Treatment with nitrous acid converts it into leucic acid, $C_6H_{12}O_3$.

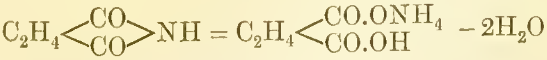
AMIDES DERIVED FROM DIATOMIC AND BIBASIC ACIDS, $C_nH_{2n}<\begin{matrix}CO_2H\\CO_2H\end{matrix}$

Each acid of this group may give rise to three amides, viz.:— 1. An acid amide or amic acid, derived from the acid ammonium salt by abstraction of one molecule of water. 2. A neutral monamide, or imide, derived from the same salt by abstraction of $2H_2O$. 3. A neutral amide, or diamide, derived from the neutral ammonium salt by abstraction of $2H_2O$; thus from succinic acid, $C_2H_4(CO_2H)_2$, are derived:

1. Succinamic acid, 

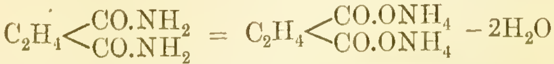
$$C_2H_4<\begin{matrix}CO.NH_2\\CO.OH\end{matrix} = C_2H_4<\begin{matrix}CO.ONH_4\\CO.OH\end{matrix} - H_2O$$

Acid Ammonium succinate.

2. Succinimide, . 

$$C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NH = C_2H_4<\begin{matrix}CO.ONH_4\\CO.OH\end{matrix} - 2H_2O$$

Acid Ammonium succinate.

3. Succinamide, . 

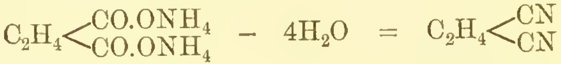
$$C_2H_4<\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix} = C_2H_4<\begin{matrix}CO.ONH_4\\CO.ONH_4\end{matrix} - 2H_2O$$

Neutral Ammonium succinate.

The two neutral amides may also be regarded as derived from one or two molecules of ammonia by substitution of the diatomic radicle of the acid for two atoms of hydrogen, and the amic acid by similar substitution in the compound molecule, $NH_3.HHO$:

Succinimide, . .	$NH.C_4H_4O_2$
Succinamide, . .	$N_2H_4.C_4H_4O_2$
Succinamic acid, . .	$\left.\begin{matrix}NH_2\\OH\end{matrix}\right\}C_4H_4O_2$.

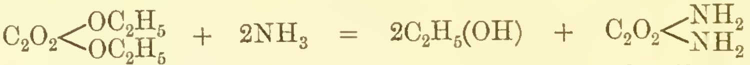
By abstraction of four molecules of water from the neutral ammonium salts, nitrils or cyanides of the corresponding diatomic alcohol-radicles are produced:



$$C_2H_4{<}\begin{matrix}CO.ONH_4\\CO.ONH_4\end{matrix} - 4H_2O = C_2H_4{<}\begin{matrix}CN\\CN\end{matrix}$$

Neutral Ammonium succinate. Succinonitril or Ethene cyanide.

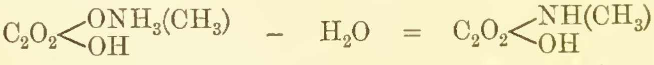
The amic acids of this group are also formed by boiling the imides with water: thus succinimide, $C_4H_5NO_2$, by taking up H_2O is converted into succinamic acid, $C_4H_7NO_3$; and the neutral amides are formed by shaking up the corresponding neutral ethers with aqueous ammonia: *e.g.*,



$$C_2O_2{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + 2NH_3 = 2C_2H_5(OH) + C_2O_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}$$

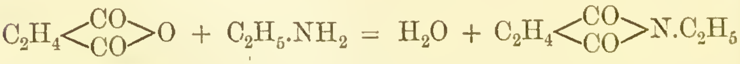
Diethylic oxalate. Ethyl alcohol. Oxamide.

The typic or extra-radical hydrogen in these amides may be replaced by alcoholic or by acid radicles, thereby producing alkalamides, secondary and tertiary diamides, &c. The modes of producing such compounds may be understood from the following equations:



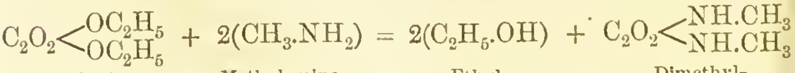
$$C_2O_2{<}\begin{matrix}ONH_3(CH_3)\\OH\end{matrix} - H_2O = C_2O_2{<}\begin{matrix}NH(CH_3)\\OH\end{matrix}$$

Acid Methylammonium oxalate. Methyloxamic acid.



$$C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O + C_2H_5.NH_2 = H_2O + C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N.C_2H_5$$

Succinic anhydride. Ethylamine. Ethyl-succinimide.

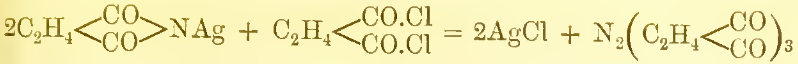


$$C_2O_2{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + 2(CH_3.NH_2) = 2(C_2H_5.OH) + C_2O_2{<}\begin{matrix}NH.CH_3\\NH.CH_3\end{matrix}$$

Diethylic oxalate. Methylamine. Ethyl alcohol. Dimethyl-oxamide.

$$COCl_2 + 2(C_2H_5.NH_2) = 2HCl + CO(NH.C_2H_5)_2$$

Carbonyl chloride. Ethylamine. Diethyl-carbamide.



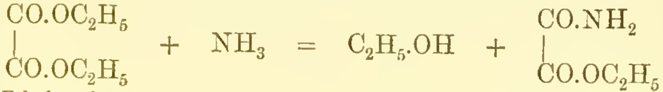
$$2C_2H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NAg + C_2H_4\left<\begin{matrix}CO.Cl\\CO.Cl\end{matrix}\right. = 2AgCl + N_2\left(C_2H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>\right)_3$$

Argento-succinimide. Succinyl chloride. Trisuccinimide.

Amides of Oxalic Acid.

Oxamic Acid, $C_2H_3NO_3 = \begin{matrix}CO.NH_2\\|\\CO.OH\end{matrix}$, is produced by heating acid ammonium oxalate to about 230°; also as an ammonium-salt by boiling oxamide with aqueous ammonia: $C_2H_4N_2O_2 + H_2O = C_2H_2(NH_4)NO_3$. Oxamic acid is a white crystalline powder sparingly soluble in cold water, still less soluble in alcohol and ether. It is monobasic, and forms numerous crystalline metallic salts.

Oxamic ethers may be formed by substitution of alcohol-radicles for hydrogen, either in the group NH_2 or in the group OH of oxamic acid, the resulting ethers being acid in the former case, neutral in the latter. The neutral ethers, also called oxamethanes, are formed by the action of ammonia, in the gaseous state or in alcoholic solution, on neutral oxalic ethers; thus:

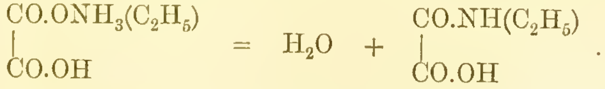


$$\begin{matrix}CO.OC_2H_5\\|\\CO.OC_2H_5\end{matrix} + NH_3 = C_2H_5.OH + \begin{matrix}CO.NH_2\\|\\CO.OC_2H_5\end{matrix}$$

Ethyl oxalate. Alcohol. Ethyl oxamate.

They are crystalline bodies soluble in alcohol, decomposed by boiling water, yielding ammonium oxalate and the corresponding alcohol.

The acid ethers of oxamic acid containing one equivalent of alcohol-radicle, are produced by dehydration of the acid oxalates of the corresponding amines; thus:



$$\begin{matrix}CO.ONH_3(C_2H_5)\\|\\CO.OH\end{matrix} = H_2O + \begin{matrix}CO.NH(C_2H_5)\\|\\CO.OH\end{matrix}.$$

Acid ethylammonium oxalate. Ethyloxamic acid.

Methyloxamic and phenyloxamic acids are also known. These acid ethers are metameric with the neutral oxamic ethers containing the same alcohol-radicles.

The replacement of both the hydrogen-atoms in the group NH_2 in oxamic acid, would also yield monobasic acid ethers; none of these are, however, known in the free state, but the ethylic ethers of dimethyl- and diethyl-oxamic acids have been obtained, *e.g.*, *ethylic dimethyl-oxamate*, $(C_2O_2)N(CH_3)_2(OC_2H_5)$.

Oxamide, $N_2H_4(C_2O_2) = \begin{matrix}CO.NH_2\\|\\CO.NH_2\end{matrix}$.—This compound is formed by the action of heat on neutral ammonium oxalate, but is more advantageously prepared by the action of ammonia on neutral ethyl oxalate. It is also formed in several reactions from cyanogen and cyanides; an aqueous solution of hydrocyanic acid, mixed with hydrogen dioxide, yields a crystalline deposit of oxamide: $2CNH + H_2O_2 = C_2N_2H_4O_2$.

Oxamide is a white, light, tasteless powder, insoluble in cold water, slightly soluble in boiling water, insoluble in alcohol. Heated in an open tube it volatilises and forms a crystalline sublimate; but its vapour, passed through a red-hot tube, is completely resolved into carbon monoxide, ammonium carbonate, hydrocyanic acid, and urea (carbamide):

$$2C_2N_2H_4O_2 = CO + CO_2 + NH_3 + CNH + CN_2H_4O.$$

Dilute mineral acids decompose it, yielding an ammonium-salt and free oxalic acid; *e.g.*,

$$C_2N_2H_4O_2 + SO_4H_2 + 2H_2O = SO_4(NH_4)_2 + C_2H_2O_4.$$

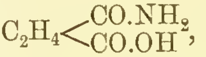
Dimethyloxamide, $N_2(C_2O_2)H_2(CH_3)_2$, is produced by the dry distillation of methylammonium oxalate:

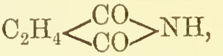
$$C_2(NH_3.CH_3)_2O_4 - 2H_2O = C_2N_2H_2(CH_3)_2O_2.$$

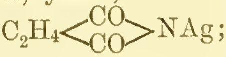
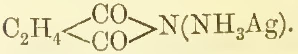
Diethyloxamide and diamyloxamide are obtained in a similar manner.

The imide of oxalic acid is not known; its nitril is dicyanogen, C_2N_2.

Amides of Succinic Acid.

Succinamic Acid,  $C_2H_4<\begin{matrix}CO.NH_2\\CO.OH\end{matrix}$, formed by heating succinimide with baryta-water, is crystalline, and is easily resolved by the action of alkalis into succinic acid and ammonia.

Succinimide,  $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NH$, formed by heating succinic anhydride in a stream of dry ammonia, or by distillation of acid ammonium succinate, crystallises in rhombic plates containing one molecule of water, dissolves easily in water and in alcohol, melts at 126°, and boils at 288°.

A hot alcoholic solution of succinimide mixed with a little ammonia and then with silver nitrate, yields, on cooling, large crystals of argentic succinimide,  $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NAg$; and the solution of this salt in a small quantity of ammonia leaves, on spontaneous evaporation, a syrupy liquid, which gradually solidifies to a mass of hard, brittle crystals of argentammonium-succinimide,  $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>N(NH_3Ag)$.

The acid character of succinimide exhibited in these salts is likewise shown by other imides, the group NH, when associated with

CO (as in cyanic acid, CO=NH) or with C_2O_2, as in the salts above described, being capable of exchanging its hydrogen for metals, like the group OH in acids.

Succinamide, $C_2H_4(CO.NH_2)_2$, separates as a white powder when neutral ammonium succinate is shaken up with aqueous ammonia. It is insoluble in cold water and alcohol, but dissolves in hot water, and separates therefrom in slender needles. At 200° it is resolved into ammonia and succinamide.

Amides of Carbonic Acid.

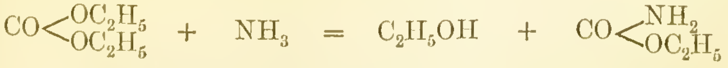
Carbamic Acid, $CO{<}{}^{NH_2}_{OH}$, is not known in the free state, that is as a hydrogen-salt, but its ammonium-salt, $(CO)(NH_2)(ONH_4)$, enters into the composition of commercial carbonate of ammonia, and is produced, as already noticed (i. 362), by the direct combination of carbon dioxide and ammonia-gas. This salt is easily obtained pure and in large quantity by passing the two gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol in a sealed tube to 100°, or above.* The liquid, on cooling, deposits ammonium carbamate in large crystalline laminæ, which, if perfectly dried over oil of vitriol, and then heated in a sealed tube to 130°–140°, split up into ammonium carbonate and carbamide, one molecule of it giving up a molecule of water to another:

$$\underset{\text{Ammonium carbamate.}}{2CN_2H_6O_2} = \underset{\text{Carbamide.}}{CN_2H_4O} + \underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3}$$

CARBAMIC ETHERS. — Carbamic acid forms acid and neutral ethers, accordingly as an atom of hydrogen in the group NH_2 or OH is replaced by an alcohol-radicle.

Ethylcarbamic acid, $CO{<}{}^{NH.C_2H_5}_{OH}$, is not known in the free state, but its ethylammonium-salt, $(CO).NH(C_2H_5).ONH_3(C_2H_5)$, is produced, as a snow-white powder, by passing carbon dioxide into anhydrous ethylamine cooled by a freezing mixture. Its aqueous solution, like that of ammonium carbamate, does not precipitate barium chloride unless aided by heat. The methylammonium-salt of *methylcarbamic acid* is obtained in a similar manner.

The neutral carbamic ethers are called **urethanes**. *Ethyl carbamate,* called simply *urethane,* is produced: 1. By leaving ethyl carbonate in contact with aqueous ammonia:



$$CO{<}{}^{OC_2H_5}_{OC_2H_5} + NH_3 = C_2H_5OH + CO{<}{}^{NH_2}_{OC_2H_5}.$$

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* Kolbe and Basaroff, Chem. Soc. Journal [2], vi. 194.

2. By the action of ammonia on ethyl chlorocarbonate (alcohol saturated with phosgene):

$$\mathrm{CO}{<}\substack{\mathrm{Cl}\\ \mathrm{OC_2H_5}} \quad + \quad \mathrm{NH_3} \quad = \quad \mathrm{HCl} \quad + \quad \mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{OC_2H_5}}$$

3. By passing cyanogen chloride into alcohol:

$$\mathrm{CNCl} \quad + \quad \mathrm{2C_2H_5(OH)} \quad = \quad \mathrm{C_2H_5Cl} \quad + \quad \mathrm{CO}{<}\substack{\mathrm{NH_3}\\ \mathrm{OC_2H_5}} .$$

4. By direct union of cyanic acid with alcohol:

$$\mathrm{CONH} \quad + \quad \mathrm{C_2H_5.OH} \quad = \quad \mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{OC_2H_5}} .$$

This compound crystallises in large tables, melts somewhat below 100°, boils at 180°; dissolves easily in water, alcohol, and ether. It is decomposed by alkalis into carbon dioxide, ammonia, and alcohol, and by ammonia into alcohol and carbamide:

$$\mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{OC_2H_5}} \quad + \quad \mathrm{NH_3} \quad = \quad \mathrm{C_2H_5OH} \quad + \quad \mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{NH_2}} .$$

The other urethanes homologous with ethyl carbonate, are obtained by similar reactions, and exhibit similar properties and decompositions. The methyl-compound, $\mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{OCH_3}}$, forms tabular crystals, melts at 52°, and boils at 177°. The isopentyl-compound, $\mathrm{CO}{<}\substack{\mathrm{NH_2}\\ \mathrm{OC_5H_{11}}}$, crystallises from hot water in needles having a metallic lustre, melts at 66°, and boils at 220°.

Thiocarbamic acid, $\mathrm{CS}{<}\substack{\mathrm{NH_2}\\ \mathrm{SH}}$, is obtained by decomposing its ammonium salt with dilute sulphuric acid, as a reddish oil, which easily splits up into thiocyanic acid and hydrogen sulphide:

$$\mathrm{CS(NH_2)(SH)} \; = \; \mathrm{CS.NH} \; + \; \mathrm{SH_2}.$$

With water it yields cyanic acid and hydrogen sulphide:

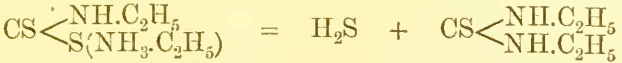
$$\mathrm{CS(NH_2)(SH)} \; + \; \mathrm{H_2O} \; = \; \mathrm{CO.NH} \; + \; \mathrm{2SH_2}.$$

Its ammonium salt, $\mathrm{CS(NH_2)(S.NH_4)}$, formed by the action of alcoholic ammonia on $\mathrm{CS_2}$, crystallises in yellowish needles or prisms.

Acid thiocarbamic ethers, or rather their amine-salts, are formed by heating carbon disulphide with amines in alcoholic solution:

$$\underset{\text{Ethylamine.}}{\mathrm{CS_2} \; + \; \mathrm{2(C_2H_5.NH_2)}} \; = \; \underset{\text{Ethylammonic ethyl-thiocarbamate.}}{\mathrm{CS}{<}\substack{\mathrm{NH.C_2H_5}\\ \mathrm{S(NH_3.C_2H_5)}}}$$

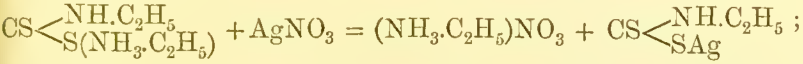
On heating this salt with caustic soda, ethylamine is separated, and sodium ethyl-thiocarbamate, $\mathrm{CS}{<}\substack{\mathrm{NH.C_2H_5}\\ \mathrm{SNa}}$, is produced, from which hydrochloric acid separates ethyl-thiocarbamic acid, $\mathrm{CS}{<}\substack{\mathrm{NH.C_2H_5}\\ \mathrm{SH}}$, as an oil which solidifies to a crystalline mass on cooling. By heating the amine salts of ethyl-thiocarbamic acid to 100°, alcoholic thiocarbamides are produced (p. 399), *e.g.*,



$$\mathrm{CS}<\genfrac{}{}{0pt}{}{\mathrm{NH.C_2H_5}}{\mathrm{S(NH_3.C_2H_5)}} \quad = \quad \mathrm{H_2S} \quad + \quad \mathrm{CS}<\genfrac{}{}{0pt}{}{\mathrm{NH.C_2H_5}}{\mathrm{NH.C_2H_5}}$$

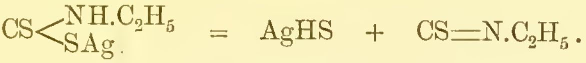
Ethylammonic Ethyl-thiocarbamate. Diethyl-thio-carbamide.

By heating the same amine-salts with metallic salts, as silver nitrate or mercuric chloride, salts of ethyl-thiocarbamic acid are precipitated: *e.g.*,



$$\mathrm{CS}<\genfrac{}{}{0pt}{}{\mathrm{NH.C_2H_5}}{\mathrm{S(NH_3.C_2H_5)}} + \mathrm{AgNO_3} = \mathrm{(NH_3.C_2H_5)NO_3} + \mathrm{CS}<\genfrac{}{}{0pt}{}{\mathrm{NH.C_2H_5}}{\mathrm{SAg}}\ ;$$

and these salts, when boiled with water, yield thiocarbimides:



$$\mathrm{CS}<\genfrac{}{}{0pt}{}{\mathrm{NH.C_2H_5}}{\mathrm{SAg}} \quad = \quad \mathrm{AgHS} \quad + \quad \mathrm{CS{=}N.C_2H_5}\,.$$

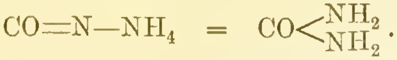
Carbimide, $\mathrm{CO{=}NH}$ or $\mathrm{N}\left\{\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{H}}\right.$, is the same as cyanic acid, and many of the reactions of cyanic acid are most appropriately represented by the formula just given, especially its resolution into carbon dioxide and ammonia under the influence of acids or alkalis:

$$\mathrm{NH(CO)} + \mathrm{H_2O} = \mathrm{NH_3} + \mathrm{CO_2}\,;$$

and the corresponding formation of ethylamine and its homologues, by distilling isocyanic ethers (alcoholic carbimides) with potash (p. 98).

In like manner thiocyanic acid or sulphocyanic acid, CNSH, is identical with thiocarbimide, $\mathrm{CS{=}NH}$, and the isothiocyanic ethers with alcoholic thiocarbimides; allyl isothiocyanate or volatile oil of mustard, for example, is the same as allyl-thiocarbimide, $\mathrm{CS{=}N.C_3H_5}$ (see THIOCYANIC ETHERS, p. 104).

Carbamide or Urea, $\mathrm{CON_2H_4} = \mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{NH_2}}$.—This compound occurs abundantly in the urine of mammalia, and in smaller quantity in that of birds and of some reptiles; also in other animal secretions. It is produced artificially: 1. By a transposition of the constituent atoms of ammonium isocyanate, which takes place when its aqueous solution is evaporated:



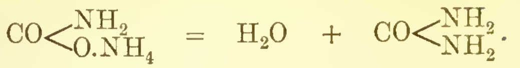
$$\mathrm{CO{=}N{-}NH_4} \quad = \quad \mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{NH_2}}\,.$$

This transformation, discovered by Wöhler in 1828, was the first instance of the artificial formation of a product of the living organism (p. 1).

2. By the action of ammonia on carbonyl chloride, or on ethylic carbonate:

$$\mathrm{COCl_2} + 2\mathrm{NH_3} = 2\mathrm{HCl} + \mathrm{CO(NH_2)_2}$$
$$\mathrm{CO(OC_2H_5)_2} + 2\mathrm{NH_3} = 2\mathrm{(C_2H_5.OH)} + \mathrm{CO(NH_2)_2}\,.$$

3. By heating ammonium carbamate to 130–140°:

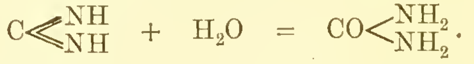


$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH_2}\\ \mathrm{O.NH_4}\end{matrix}\right. = \mathrm{H_2O} + \mathrm{CO}\left<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right..$$

4. By heating oxamide with mercuric oxide:

$$C_2O_2(NH_2)_2 + HgO = CO_2 + Hg + CO(NH_2)_2.$$

5. By the action of small quantities of acids on cyanamide:



$$\mathrm{C}\ll\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix} + \mathrm{H_2O} = \mathrm{CO}\left<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right..$$

It is also produced by the action of alkalis on creatine and allantoïn, and by oxidation of uric acid, guanine, and xanthine.

Preparation.—1. From urine. Fresh human urine is concentrated in a water-bath, until reduced to an eighth or a tenth of its original volume, and filtered through cloth from the insoluble deposit of urates and phosphates. The liquid is mixed with about an equal quantity of strong solution of oxalic acid in hot water, and the whole vigorously agitated and left to cool. A very copious fawn-coloured crystalline precipitate of *urea oxalate* is thus obtained, which may be placed upon a cloth filter, slightly washed with cold water, and pressed. This is to be dissolved in boiling water, and powdered chalk added until effervescence ceases, and the liquid becomes neutral. The solution of urea is filtered from the insoluble calcium oxalate, warmed with a little animal charcoal, again filtered, and concentrated by evaporation, avoiding ebullition, until crystals form on cooling: these are purified by a repetition of the last part of the process. Another process consists in precipitating the evaporated urine with concentrated nitric acid, when *urea nitrate* is precipitated, which is purified by recrystallisation with the aid of animal charcoal, and, lastly, decomposed by barium carbonate, whereby a mixture of barium nitrate and urea is formed, which is to be evaporated to dryness on the water-bath, and exhausted with hot alcohol; the urea then crystallises on cooling. Urea may also be extracted in great abundance from the urine of horses and cattle duly concentrated, and from which the hippuric acid has been separated by addition of hydrochloric acid; oxalic acid then throws down the oxalate in such quantity as to render the whole semi-solid.

2. From ammonium isocyanate.—Potassium isocyanate is dissolved in a small quantity of water, and a quantity of dry neutral ammonium sulphate, equal in weight to the cyanate, is added. The whole is evaporated to dryness in a water-bath, and the dry residue boiled with strong alcohol, which dissolves out the urea, leaving the potassium sulphate and the excess of ammonium sulphate untouched. The filtered solution, concentrated by distilling off a portion of the spirit, deposits the urea in beautiful crystals of considerable size. According to J. Williams,* isocyanate of lead is more convenient for this preparation than the potassium salt. It is to be digested at a

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* Chem. Soc. Journal (1868), xxi. 63.

gentle heat in a sufficient quantity of water with an equivalent quantity of ammonium sulphate, and the liquid filtered and evaporated.

Urea forms transparent, colourless, four-sided prisms, which are anhydrous, soluble in an equal weight of cold water, and in a much smaller quantity at a high temperature. It is also readily dissolved by alcohol. It is inodorous, has a cooling saline taste, and is permanent in moderately dry air. When heated it melts, and at a higher temperature decomposes, giving off ammonia and ammonium cyanate, and leaving cyanuric acid, which bears a much greater heat without change. The solution of urea is neutral to test-paper; it is not decomposed in the cold by alkalis or by calcium hydrate, but at a boiling heat emits ammonia, and forms a metallic carbonate. The same change is produced by fusion with the alkaline hydrates, and when urea is heated with water in a sealed tube to a temperature above 100°:

$$COH_4N_2 + H_2O = CO_2 + 2NH_3.$$

Urea, heated with a large excess of potassium permanganate, in presence of much free alkali, gives off all its nitrogen in the free state, differing, in this respect, from most amides, the nitrogen of which is oxidised by this treatment to nitric acid.

Urea is instantly decomposed by *nitrous acid* into carbon dioxide, nitrogen, and water: $COH_4N_2 + 2NO_2H = CO_2 + 2N_2 + 3H_2O$; this decomposition explains the use of urea in preparing nitric ether (p. 135). When *chlorine gas* is passed over melted urea, hydrochloric acid and nitrogen are evolved, and there remains a mixture of salammoniac and cyanuric acid:

$$6COH_4N_2 + 3Cl_2 = 2C_3H_3N_3O_3 + 4NH_4Cl + 2HCl + N_2.$$

A solution of pure urea shows no tendency to change by keeping, and is not decomposed by boiling; in the urine, on the other hand, where it is associated with putrefiable organic matter, as mucus, the case is different. In putrid urine no urea can be found, but enough ammonium carbonate to cause brisk effervescence with an acid; and if urine, in a recent state, be long boiled, it gives off ammonia and carbonic acid from the same source.

COMPOUNDS OF UREA.—1. With Acids.—Urea, like glycocine, unites with acids, bases, and salts, but though a diamide, it combines with only one molecule of an acid, one of its amidogen groups being neutralised by the CO- group.

The *nitrate*, $CH_4N_2O.NO_3H$, is readily soluble in water, and crystallises from the aqueous solution in long prisms, but slightly soluble in nitric acid, and is therefore precipitated by nitric acid from the aqueous solution of urea. The *oxalate*, $(CH_4N_2O)_2.C_2H_2O_4$, is obtained as a white crystalline precipitate by mixing the aqueous solutions of oxalic acid and urea; it is but slightly soluble in water.

2. With Metallic Oxides.—On adding moist *silver oxide* to a solution of urea, the compound, $COH_4N_2.3Ag_2O$, is deposited as a grey powder made up of fine needles. *Mercuric nitrate* added to a solution of urea, mixed with potash, forms a white precipitate containing $COH_4N_2.2HgO$. With *mercuric chloride* a white precipitate is formed, which, on boiling with water, turns yellow, and is converted into $COH_4N_2.3HgO$. On adding mercuric oxide to a warm solution of urea, the compound, $COH_4N_2.HgO$, appears to be produced.

3. With Salts.—On evaporating a solution of urea mixed with *sodium chloride*, the compound $COH_4N_2.NaCl$ is obtained in shining prisms. The compound $COH_4N_2.AgNO_3$ obtained in a similar manner, forms large rhombic prisms.

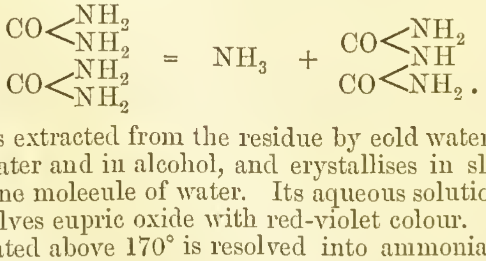
Isuretine, CH_4N_2O, isomeric with urea, is formed by direct combination of hydrogen cyanide (carbimide) with hydroxylamine: $CNH + NH_3O = CH_4N_2O$, and is obtained by evaporation in long colourless needles, having a strong alkaline reaction, and melting at 104°. Its hydrochloride, $CH_4N_2O.HCl$, forms deliquescent rhombic plates.

Isuretine decomposes above its melting-point, yielding a sublimate of ammonium carbonate, and a residue containing ammelide (p. 107. Its aqueous solution also decomposes when evaporated, giving off nitrogen, ammonia, and carbon dioxide, and leaving a residue containing urea and biuret.

The constitution of isuretine may perhaps be represented by the formula $\mathrm{CH}{<}\begin{array}{l}\mathrm{NH}\\ \mathrm{NH.OH}\end{array}$.

Hydroxyl-carbamide or **Hydroxyl-urea,** $CH_4N_2O_2 = \mathrm{CO}{<}\begin{array}{l}\mathrm{NH.OH}\\ \mathrm{NH_2}\end{array}$, is prepared by adding a strong solution of potassium cyanate to a solution of hydroxylamine nitrate cooled to −10°. It dissolves easily in water and in alcohol, and is precipitated from these solutions by ether in white needles melting at 128°–130°.

Biuret, $C_2H_5N_3O_2$, is produced by heating urea to 150°–160°, the change consisting in the separation of one molecule of ammonia from two molecules of urea:



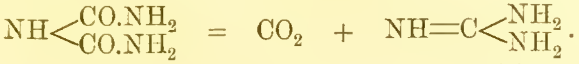
$$\begin{array}{l}\mathrm{CO}{<}\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH_2}\end{array}\\ \mathrm{CO}{<}\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH_2}\end{array}\end{array} = \mathrm{NH_3} + \begin{array}{l}\mathrm{CO}{<}\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH}\end{array}\\ \mathrm{CO}{<}\mathrm{NH_2}.\end{array}$$

The biuret is extracted from the residue by cold water. It is easily soluble in water and in alcohol, and crystallises in slender needles containing one molecule of water. Its aqueous solution, mixed with potash, dissolves cupric oxide with red-violet colour.

Biuret heated above 170° is resolved into ammonia and cyanuric acid:

$$3C_2H_5N_3O_2 = 3NH_3 + 2C_3H_3N_3O_3.$$

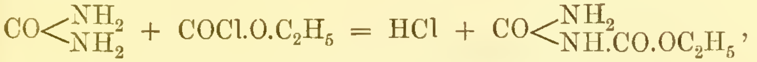
When heated in a stream of gaseous hydrogen chloride, it yields cyanuric acid, urea, and guanidine, CH_5N_3, together with ammonia and carbon dioxide. The formation of guanidine is represented by the equation:



$$\mathrm{NH}<\begin{matrix}\mathrm{CO.NH_2}\\ \mathrm{CO.NH_2}\end{matrix} = \mathrm{CO_2} + \mathrm{NH{=}C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}.$$

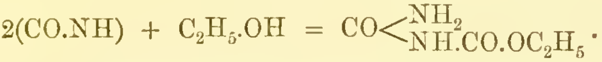
Biuret. Guanidine.

Ethyl Allophanate, $\mathrm{C_2H_3(C_2H_5)N_2O_3} = \mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.OC_2H_5}\end{matrix}$, or $\mathrm{NH}<\begin{matrix}\mathrm{CO.NH_2}\\ \mathrm{CO.OC_2H_5}\end{matrix}$, is produced by the action of ethyl chlorocarbonate on urea:



$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix} + \mathrm{COCl.O.C_2H_5} = \mathrm{HCl} + \mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.OC_2H_5}\end{matrix},$$

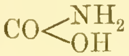
or by passing cyanic acid vapour into absolute alcohol:



$$2(\mathrm{CO.NH}) + \mathrm{C_2H_5.OH} = \mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.OC_2H_5}\end{matrix}.$$

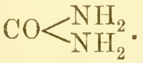
This ether forms shining prismatic crystals, soluble in hot water and in alcohol. Treated with caustic baryta, it yields the barium salt of allophanic acid, $C_2H_4N_2O_3$, but the acid itself cannot be obtained in the free state, as, when separated from the barium salt by a mineral acid, it is immediately resolved into urea and carbon dioxide. A series of allophanic ethers may, however, be prepared by the action of cyanic acid on various alcohols.

Allophanic acid is related to biuret in the same manner as carbamic acid to urea:



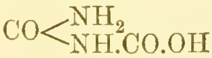
$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\end{matrix}$$

Carbamic acid.



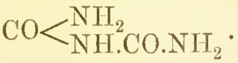
$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}.$$

Urea.



$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.OH}\end{matrix}$$

Allophanic acid.



$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.NH_2}\end{matrix}.$$

Biuret.

In other words, biuret is the amide of allophanic acid.

Trigenic Acid, $\mathrm{C_4H_7N_3O_2}{=}\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH.CO.N{=}C_2H_4}\end{matrix}$, is produced by passing cyanic acid vapour into cold aldehyde:

$$3(\mathrm{CO.NH}) + \mathrm{C_2H_4O} = \mathrm{CO_2} + \mathrm{C_4H_7N_3O_2}.$$

It crystallises in prisms slightly soluble in water and in alcohol, and decomposing when heated.

Derivatives of Carbamide.—Compound Ureas.

The hydrogen in carbamide may be replaced by alcoholic or by acid radicles.

1. The alcoholic derivatives are formed by processes similar to those which yield carbamide itself, namely, by the action of amines on cyanic acid, or of ammonia and amines on cyanic ethers:

$$CO{=}NH + NH_2.C_2H_5 = CO{<}\begin{matrix}NH.C_2H_5\\NH_2\end{matrix} \quad \text{Ethyl-carbamide.}$$

$$CO{=}N.CH_3 + NH_3 = CO{<}\begin{matrix}NH.CH_3\\NH_2\end{matrix} \quad \text{Methyl-carbamide.}$$

$$CO{=}N.C_2H_5 + NH_2.CH_3 = CO{<}\begin{matrix}NH.C_2H_5\\NH.CH_3\end{matrix} \quad \text{Methyl-ethyl-carbamide.}$$

$$CO{=}N.C_2H_5 + NH(C_2H_5)_2 = CO{<}\begin{matrix}NH.C_2H_5\\N(C_2H_5)_2\end{matrix} \quad \text{Triethyl-carbamide.}$$

They are also produced by heating isocyanic ethers with water, the reaction apparently taking place by two stages, thus:

$$CO{=}N.C_2H_5 + H_2O = CO_2 + NH_2.C_2H_5$$

and

$$CO{=}N.C_2H_5 + NH_2.C_2H_5 = CO{<}\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}.$$

These compounds greatly resemble urea in their properties and reactions. They combine with one equivalent of an acid. By boiling with alkalis they are resolved into carbon dioxide and amines.

Methyl-carbamide, $CO{<}\begin{matrix}NH.CH_3\\NH_2\end{matrix}$, crystallises in long transparent prisms. Its aqueous solution is neutral to test-paper, and if somewhat concentrated yields with nitric acid a precipitate of the salt $C_2H_6N_2O.HNO_3$.

Dimethyl-carbamide, $CO{<}\begin{matrix}NH.CH_3\\NH.CH_3\end{matrix}$, produced by the action of water or of methylamine on methyl cyanate, crystallises easily, melts at 97°, volatilises without alteration, and forms with nitric acid the salt $C_3H_8N_2O.HNO_3$.

Ethyl-carbamide, $CO{<}\begin{matrix}NH.C_2H_5\\NH_2\end{matrix}$, forms large prisms, easily soluble in water and in alcohol, melting at 92°. Nitric acid does not precipitate its aqueous solution, but crystals of the nitrate $C_2H_7N_2O.HNO_3$ are obtained on evaporation.

Diethyl-carbamide, $CON_2H_2(C_2H_5)_2$.—Of this compound there are two modifications.

α-Diethyl-carbamide, $CO{<}\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}$, formed by the action of water or of ethylamine on ethyl cyanate (see above), crystallises in long prisms, melts at 112°, and boils without decomposition at 263°.

β-Diethyl-carbamide, $\mathrm{CO}<^{\mathrm{N(C_2H_5)_2}}_{\mathrm{NH_2}}$, is formed by the action of diethylamine on cyanic acid:

$$\mathrm{CO{=}NH} + \mathrm{NH(C_2H_5)_2} = \mathrm{CO}<^{\mathrm{N(C_2H_5)_2}}_{\mathrm{NH_2}}.$$

It melts at 97°, and boils at 270°–280°.

Methyl-ethyl-carbamide, $\mathrm{CO}<^{\mathrm{NH.CH_3}}_{\mathrm{NH.C_2H_5}}$, formed by the action of methylamine on ethyl isocyanate, is very deliquescent.

Triethyl-carbamide, $\mathrm{CO}<^{\mathrm{N.(C_2H_5)_2}}_{\mathrm{NH.C_2H_5}}$, is easily soluble in water, alcohol, and ether, melts at 53°, and distils at 223°.

Allyl-carbamide, $\mathrm{CO}<^{\mathrm{NH.C_3H_5}}_{\mathrm{NH_2}}$, from allyl isocyanate and ammonia, crystallises in fine prisms.

Diallyl-carbamide or *Sinapoline*, $\mathrm{CO}<^{\mathrm{NH.C_3H_5}}_{\mathrm{NH.C_3H_5}}$, is formed by heating allyl isocyanate with water:

$$2(\mathrm{CO{=}N.C_3H_5}) + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{CO(NH.C_3H_5)_2},$$

or by heating allyl-isothiocyanate, $\mathrm{CS{=}N.C_3H_5}$, (volatile oil of mustard) with water and lead oxide, whereby diallyl-thiocarbamide, $\mathrm{CS(NH.C_3H_5)_2}$, is first produced. and then converted into diallyl-carbamide by the action of the lead oxide. Diallyl-carbamide crystallises in large shining laminæ, slightly soluble in water, having an alkaline reaction, and melting at 100°.

Ethene-dicarbamide, $\mathrm{C_4H_{10}N_4O_2} = \mathrm{C_2H_4}<^{\mathrm{NH{-}CO{-}NH_2}}_{\mathrm{NH{-}CO{-}NH_2}}$, is formed by heating ethene-diamine hydrochloride with silver cyanate:

$$\mathrm{C_2H_4(NH_2)_2.2HCl} + \mathrm{2CNOAg} = \mathrm{2AgCl} + \mathrm{C_2O_2(NH_2)_2(NH)_2.C_2H_4}.$$

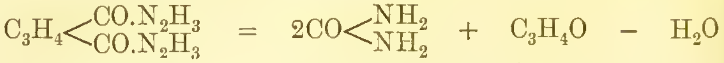
It is sparingly soluble in alcohol, easily in hot water, melts with decomposition at 192°.

Diethyl-ethene-carbodiamide, $\mathrm{C_2O_2(NH.C_2H_5)_2(NH)_2(C_2H_4)}$, admits of two modifications, viz.:

$$\mathrm{C_2H_4}<^{\mathrm{NH{-}CO{-}NH(C_2H_5)}}_{\mathrm{NH{-}CO{-}NH(C_2H_5)}} \text{ and } \mathrm{C_2H_4}<^{\mathrm{N(C_2H_5){-}CO{-}NH_2}}_{\mathrm{N(C_2H_5){-}CO{-}NH_2}},$$

the first produced from ethyl isocyanate and ethene-diamine, the second from cyanic acid and diethyl-ethene-diamine.

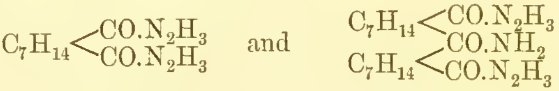
Alcoholic carbamides containing diatomic radicles are also produced by combination of carbamides with aldehydes, with elimination of water; *e.g.*,



$$C_3H_4{<}\begin{matrix}CO.N_2H_3\\CO.N_2H_3\end{matrix} = 2CO{<}\begin{matrix}NH_2\\NH_2\end{matrix} + C_3H_4O - H_2O$$

Allylene-di-carbamide. Carbamide. Acrolein.

In like manner the compounds,



$$C_7H_{14}{<}\begin{matrix}CO.N_2H_3\\CO.N_2H_3\end{matrix} \quad \text{and} \quad \begin{array}{l}C_7H_{14}{<}CO.N_2H_3\\ \qquad\quad CO.NH_2\\C_7H_{14}{<}CO.N_2H_3\end{array}$$

Heptene-dicarbamide. Diheptene-tricarbamide.

are produced from carbamide and œnanthol. All these aldehydic carbamides are resolved by boiling with water into carbamide and aldehyde.

2. Containing Acid Radicles.—Carbamides containing monatomic acid radicles are formed by the action of acid chlorides or anhydrides on carbamide. They are not capable of forming salts with acids. Alkalis decompose them into carbamide and the corresponding acid.

Acetyl-carbamide, $CO{<}\begin{matrix}NH.C_2H_3O\\NH_2\end{matrix}$, crystallises in long, silky needles, melting at 112°, slightly soluble in cold water and alcohol, decomposed by heating into acetamide and cyanuric acid.—*Chloracetyl-carbamide*, $C_3H_5ClN_2O_2 = CO(NH_2)(NH.C_2H_2ClO)$, forms laminæ easily soluble in water, and is resolved by heat into hydrochloric acid and hydantoïn, $C_3H_4N_2O_2$.—*Bromacetyl-carbamide*, $C_3H_5BrN_2O_2$, crystallises in needles slightly soluble in water, and is decomposed by heat in a similar manner.

Diacetyl-carbamide, $CO(NH.C_2H_3O)_2$, produced by the action of acetic anhydride on carbamide, or of carbonyl chloride on acetamide, crystallises in needles, and sublimes without decomposition.

Carbamides containing diatomic acid radicles, such as *glycolyl-carbamide*, $CO{<}\begin{matrix}NH\\NH\end{matrix}{>}C_2H_2O$, are obtained as derivatives of uric acid, and will be described in connection therewith.

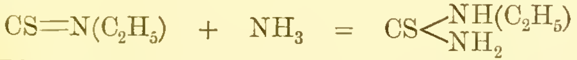
Thiocarbamide or Thio-urea, $CS{<}\begin{matrix}NH_2\\NH_2\end{matrix}$, also called *Sulphocarbamide* and *Sulphurea*.—This compound is formed by heating ammonium thiocyanate to 170° in the same manner as carbamide is formed from ammonium cyanate. It crystallises in silky needles or thick rhombic prisms, easily soluble in water and alcohol, sparingly in ether, melts at 146°, and decomposes at a higher temperature, giving off carbon disulphide, hydrogen sulphide, and ammonia, and leaving melam (p. 107). When heated with water to 140° it is reconverted into ammonium sulphocyanate, and by boiling with alkalis, or with hydrochloric or sulphuric acid, it is decomposed according to the equation:

$$CSN_2H_4 + 2H_2O = CO_2 + 2NH_3 + H_2S.$$

In contact with the oxides of silver, mercury, or lead, and water, it is converted at ordinary temperatures into cyanamide, $CN.NH_2$, and by boiling into dicyanodiamide, $C_2N_4H_4$ (p. 106).

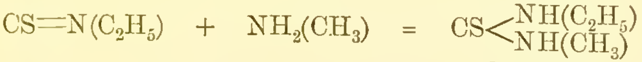
Thiocarbamide, like carbamide, forms salts containing one equivalent of acid. The *nitrate*, $CSN_2H_4.HNO_3$, forms large crystals.

Alcoholic derivatives of thiocarbamide are formed by processes similar to those employed in the preparation of the alcoholic carbamides; *e.g.*,



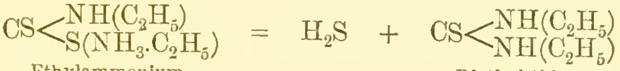
$$CS{=}N(C_2H_5) + NH_3 = CS{<}\begin{matrix}NH(C_2H_5)\\ NH_2\end{matrix}$$

Ethyl thiocyanate. Ethyl-thiocarbamide.



$$CS{=}N(C_2H_5) + NH_2(CH_3) = CS{<}\begin{matrix}NH(C_2H_5)\\ NH(CH_3)\end{matrix}$$

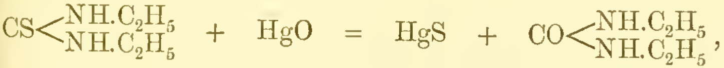
Methyl-ethyl-thiocarbamide.



$$CS{<}\begin{matrix}NH(C_2H_5)\\ S(NH_3.C_2H_5)\end{matrix} = H_2S + CS{<}\begin{matrix}NH(C_2H_5)\\ NH(C_2H_5)\end{matrix}$$

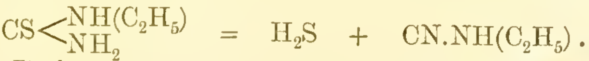
Ethylammonium Ethyldithiocarbamate. Diethyl-thiocarbamide.

These compounds are desulphurised by heating them with water and mercuric oxide, the sulphur being replaced by oxygen. Those containing two equivalents of alcohol-radicle are converted by this reaction into the corresponding carbamides:



$$CS{<}\begin{matrix}NH.C_2H_5\\ NH.C_2H_5\end{matrix} + HgO = HgS + CO{<}\begin{matrix}NH.C_2H_5\\ NH.C_2H_5\end{matrix},$$

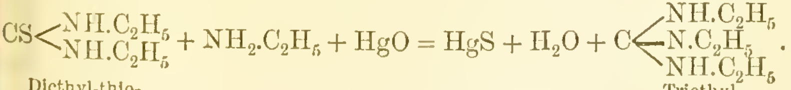
whereas the mono-substituted derivatives are converted, by further separation of hydrogen sulphide, into alcoholic cyanamides (melamines, p. 107):



$$CS{<}\begin{matrix}NH(C_2H_5)\\ NH_2\end{matrix} = H_2S + CN.NH(C_2H_5).$$

Ethyl-thiocarbamide. Ethyl-cyanamide.

When the bisubstituted thiocarbamides are heated with mercuric oxide and amines, the oxygen of the substituted carbamide formed in the first instance is replaced by imidogen, NH, and substituted guanidines are produced; thus:



$$CS{<}\begin{matrix}NH.C_2H_5\\ NH.C_2H_5\end{matrix} + NH_2.C_2H_5 + HgO = HgS + H_2O + C{\leftarrow}\begin{matrix}NH.C_2H_5\\ N.C_2H_5\\ NH.C_2H_5\end{matrix}.$$

Diethyl-thiocarbamide. Triethyl-guanadine.

Ethyl-thiocarbamide, $CS(NH_2)(NH.C_2H_5)$, crystallises in needles melting at 89°. *Diethyl-thiocarbamide*, $CS(NH.C_2H_5)_2$, forms large crystals sparingly soluble in water, and melting at 77°. *Methylethyl-thiocarbamide*, $CS(NH.CH_3)(NH.C_2H_5)$, melts at 54°.

Allyl-thiocarbamide, or *Thiosinnamine*, $CS\Big<\begin{matrix}NH.C_3H_5\\NH_2\end{matrix}$, obtained by combination of allylthiocarbimide (mustard-oil) with ammonia:

$$CS{=}N.C_3H_5 + NH_3 = CS\Big<\begin{matrix}NH.C_3H_5\\NH_2\end{matrix},$$

crystallises in shining rhombic prisms, having a bitter taste, melting at 70°, and decomposing at a higher temperature; easily soluble in water, alcohol, and ether. Its salts are decomposed by water. By boiling with mercuric oxide or lead oxide and water, it is converted into allyl-cyanamide, $CN.NH.C_3H_5$, which is then further converted, as above explained, into triallylmelamine or sinnamine, $C_3N_3(NH.C_3H_5)_3$.

CARBAMIDES CONTAINING DIATOMIC ACID RADICLES:—

URIC ACID AND UREIDES.

Uric Acid, $C_5N_4H_4O_3$, formerly called *Lithic acid*, is a product of the animal organism, and has never been formed by artificial means. It may be prepared from human urine by concentration and addition of hydrochloric acid, and crystallises out after some time in the form of small, reddish, translucent grains, very difficult to purify. A much preferable method is to employ the solid white excrement of serpents, which can be easily procured: this consists almost entirely of uric acid and ammonium urate. It is reduced to powder, and boiled in dilute solution of caustic potash; the liquid, filtered from the insignificant residue of feculent matter and earthy phosphates, is mixed with excess of hydrochloric acid, boiled for a few minutes, and left to cool. The product is collected on a filter, washed until free from potassium chloride, and dried by gentle heat.

Uric acid, thus obtained, forms a glistening, snow-white powder, tasteless, inodorous, and very sparingly soluble. It is seen under the microscope to consist of minute, but regular crystals. It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. By destructive distillation, uric acid yields cyanic acid, hydrocyanic acid, carbon dioxide, ammonium carbonate, and a black coaly residue, rich in nitrogen. By fusion with potassium hydroxide, it yields potassium carbonate, cyanate, and cyanide. When treated with nitric acid and with lead dioxide, it undergoes decomposition in a manner to be presently described.

Uric acid is bibasic: its most important salts are those of the alkali-metals. *Acid potassium urate*, $C_5N_4H_3KO_3$, is deposited from a hot saturated solution of uric acid in the dilute alkali, as a white, sparingly soluble, concrete mass, composed of minute needles: it requires about 500 parts of cold water for solution, is rather more soluble at a high temperature, and much more soluble in excess of alkali. *Sodium urate* resembles the potassium-salt: it forms the chief constituent of the gouty concretions in the joints, called *chalk-stones*. *Ammonium urate* is also a sparingly soluble compound, requiring for solution about 1000 parts of cold water: the solubility is very much increased by the presence of a small quantity of certain salts, as sodium chloride. The most common of the urinary deposits, forming a buff-coloured or pinkish cloud or muddiness, which disappears by redissolution when the urine is warmed, consists of a mixture of different urates.

Uric acid is perfectly well characterised, even when in very small quantity, by its behaviour with nitric acid. A small portion, mixed with a drop or two of nitric acid in a small porcelain capsule, dissolves with copious effervescence. When this solution is cautiously evaporated nearly to dryness, and, after the addition of a little water, mixed with a slight excess of ammonia, a deep-red tint of murexide is immediately produced.

Impure uric acid, in a more or less advanced state of decomposition, is imported into this country, in large quantities, for use as a manure, under the name of *guano* or *huano*. It comes chiefly from the barren and uninhabited islets of the western coast of South America, and is the production of the countless birds that dwell undisturbed in those regions. The people of Peru have used it for ages. Guano usually appears as a pale-brown powder, sometimes with whitish specks; it has an extremely offensive odour, the strength of which, however, varies very much. It is soluble in great part in water, and the solution is found to be extremely rich in ammonium oxalate, the acid having been generated by a process of oxidation. Guano also contains a base called guanine.

Products formed from Uric Acid by Oxidation, &c.

When uric acid is subjected to the action of an oxidising agent in presence of water, it gives up two of its hydrogen-atoms to the oxidising agent, while the dehydrogenised residue (which may be called dehyduric acid) reacts with water to form mesoxalic acid and urea:

$$\underset{\text{Dehyduric acid.}}{C_5H_2N_4O_3} + 4H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_2O_5} + \underset{\text{Urea.}}{2CH_4N_2O}$$

The separation of the urea generally takes place, however, by two stages, the first portion being removed more easily than the second; thus, when dilute nitric acid acts upon uric acid, alloxan is produced; and this, when heated with baryta-water, is further resolved into mesoxalic acid and urea:

$$\underset{\text{Dehyduric acid.}}{C_5N_4H_2O_3} + 2H_2O = \underset{\text{Alloxan.}}{C_4N_2H_2O_4} + \underset{\text{Urea.}}{CN_2H_4O}$$

$$\underset{\text{Alloxan.}}{C_4N_2H_2O_4} + 2H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_2O_5} + \underset{\text{Urea.}}{CN_2H_4O}$$

Alloxan is a *monureide* of mesoxalic acid—that is to say, it is a compound of that acid with one molecule of urea minus $2H_2O$; and the hypothetical dehyduric acid is the *diureide* of the same acid, derived from it by addition of 2 molecules of urea and subtraction of 4 molecules of water. Now, by hydrogenising mesoxalic acid, we obtain tartronic acid, $C_3H_4O_5$ (p. 358); and by hydrogenising alloxan, we obtain dialuric acid, which two bodies, accordingly, bear to uric acid the same relation that mesoxalic acid and urea bear to dehyduric acid; thus:

$C_3H_2O_5$ Mesoxalic acid.	$C_4N_2H_2O_4$ Alloxan.	$C_5N_4H_2O_3$ Dehyduric acid.
$C_3H_4O_5$ Tartronic acid.	$C_4N_2H_4O_4$ Dialuric acid.	$C_5N_4H_4O_3$; Uric acid.

and just as the hypothetical dehyduric acid yields mesoxalic acid and alloxan, so should actual uric acid yield tartronic and dialuric acids. These bodies, however, have not been obtained by the direct breaking-up of uric acid, but only by rehydrogenising the mesoxalic acid and alloxan which result from the breaking-up of its dehydrogenised product. Provisionally, however, dialuric and uric acids may be regarded as tartron-ureide and tartron-diureide respectively:

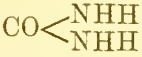
$$\underset{\text{Tartronic acid.}}{C_3H_4O_3} + \underset{\text{Urea.}}{CH_4N_2O} - 2H_2O = \underset{\text{Dialuric acid.}}{C_4H_4N_2O_4}$$

$$\underset{\text{Tartronic acid.}}{C_3H_4O_5} + \underset{\text{Urea.}}{2CH_4N_2O} - 4H_2O = \underset{\text{Uric acid.}}{C_5H_4N_4O_3}.$$

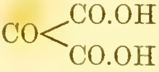
The bodies just mentioned may be regarded as typical of three well-defined classes of compounds, to one or other of which a very large number of uric acid products may be referred, viz.: (1). Non-azotised bibasic acids, such as mesoxalic and tartronic acid; (2). Monureides, such as dialuric acid and alloxan, containing a residue or radicle of such an acid, *e.g.*, mesoxalyl, C_3H_3 plus one urea-residue, $CO<\begin{matrix}NH\\NH\end{matrix}$; (3). Diureides, such as uric acid itself, containing an acid residue together with two urea-residues.

Monureides.

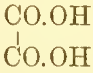
These compounds may be regarded as carbamides or ureas, in which part of the hydrogen (generally half) is replaced by diatomic acid radicles. They are either 4-carbon compounds belonging to the mesoxalic series, and containing the radicle $\begin{matrix}CO\\CO\end{matrix}>CO$(mesoxalyl), or radicles derived from it,—or 3-carbon compounds belonging to the oxalic series, and containing the radicle CO—CO (oxalyl), or others derived therefrom. These relations are exhibited in the following table:


$CO<\begin{matrix}NHH\\NHH\end{matrix}$

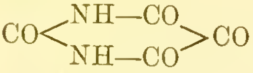
Urea.


$CO<\begin{matrix}CO.OH\\CO.OH\end{matrix}$

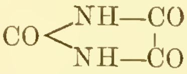
Mesoxalic acid.


$\begin{matrix}CO.OH\\|\\CO.OH\end{matrix}$

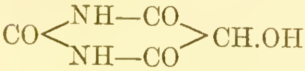
Oxalic acid.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CO$

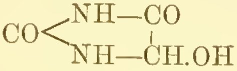
Mesoxalyl-urea
Alloxan.


$CO<\begin{matrix}NH—CO\\|\\NH—CO\end{matrix}$

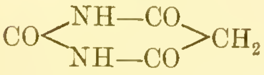
Oxalyl-urea
Parabanic acid.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CH.OH$

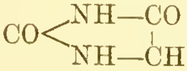
Tartronyl-urea
Dialuric acid.


$CO<\begin{matrix}NH—CO\\|\\NH—CH.OH\end{matrix}$

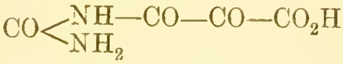
Oxyglycolyl-urea
Allanturic acid.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CH_2$

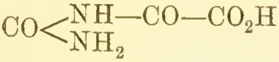
Malonyl-urea
Barbituric acid.


$CO<\begin{matrix}NH—CO\\|\\NH—CH\end{matrix}$

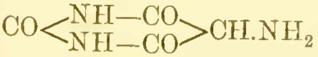
Glycolyl-urea
Hydantoïn.


$CO<\begin{matrix}NH—CO—CO—CO_2H\\NH_2\end{matrix}$

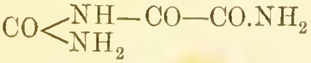
Alloxanic acid.


$CO<\begin{matrix}NH—CO—CO_2H\\NH_2\end{matrix}$

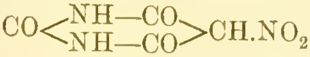
Oxaluric acid.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CH.NH_2$

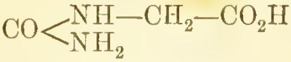
Amidobarbituric acid
Uramil.


$CO<\begin{matrix}NH—CO—CO.NH_2\\NH_2\end{matrix}$

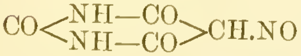
Oxaluramide.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CH.NO_2$

Nitrobarbituric acid,
Dilituric acid.


$CO<\begin{matrix}NH—CH_2—CO_2H\\NH_2\end{matrix}$

Hydantoïn or
Glycoluric acid.


$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>CH.NO$

Nitrosobarbituric acid.

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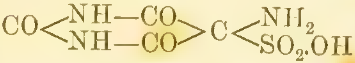

$CO<\begin{matrix}NH—CO\\NH—CO\end{matrix}>C<\begin{matrix}NH_2\\SO_2.OH\end{matrix}$

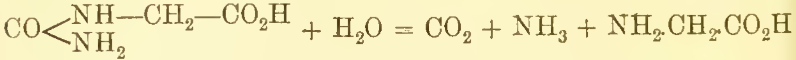
Thionuric acid.

......

Most of these compounds, when treated with alkalis, are resolved into the corresponding diatomic acids and urea, or its products of decomposition: *e.g.*,

$$\underset{\text{Alloxan.}}{C_4H_2N_2O} + 2H_2O = \underset{\text{Mesoxalic acid.}}{C_3O_2(OH)_2} + \underset{\text{Urea.}}{CON_2H_4}$$

Those which contain the group NH, united with CH_2, are converted by boiling with alkalis, or with strong hydriodic acid, into amido-acids:



$$\underset{\text{Glycoluric acid.}}{CO{<}{\begin{matrix}NH{-}CH_2{-}CO_2H\\NH_2\end{matrix}}} + H_2O = CO_2 + NH_3 + \underset{\text{Glycocine.}}{NH_2.CH_2.CO_2H}$$

1. Mesoxalic Series.

Alloxan, $C_4H_2N_2O_4$.—This is the characteristic product of the action of strong nitric acid on uric acid in the cold. It is best prepared by adding 1 part of pulverised uric acid to 3 parts of nitric acid, specific gravity 1·45, in a shallow basin standing in cold water. The resulting white crystalline mass, after standing for some hours, is drained from the acid liquid in a funnel having its neck stopped with pounded glass, then dried on a porous tile, and purified by crystallisation from a small quantity of water.

Alloxan crystallises by slow cooling from a hot saturated solution in large efflorescent rectangular prisms containing $C_4H_2N_2O_4 + 4$ aq.; from a solution evaporated by heat it separates in monoclinic octohedrons with truncated summits, containing $C_4H_2N_2O_4 +$ aq. These crystals heated to 150°–160° in a stream of hydrogen give off their water, and leave anhydrous alloxan, $C_4N_2H_2O_4$. Alloxan is very soluble in water: the solution has an acid reaction, a disagreeably astringent taste, and stains the skin, after a time, red or purple. It forms a deep-blue compound with a ferrous salt and an alkali, and its solution, mixed with hydrocyanic acid and ammonia, yields a white precipitate of oxaluramide; these two reactions are very characteristic.

Alloxan unites (like ketones) with alkaline bisulphites, forming crystalline compounds.

Its aqueous solution decomposes gradually at ordinary temperatures, more quickly on boiling, into alloxantin, parabanic acid, and carbon dioxide:

$$\underset{\text{Alloxan.}}{3C_4H_2N_2O_4} = \underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + \underset{\text{Parabanic acid}}{C_3H_2N_2O_3} + CO_2$$

By boiling with dilute acids, alloxan is resolved into oxalic acid and urea; by boiling with baryta-water or lead acetate, it is first converted into alloxanic acid, which then splits up into urea and mesoxalic acid. By hydriodic acid and other reducing agents, alloxan is converted, especially in the cold, into alloxantin; at higher temperatures into dialuric acid.

Alloxanic Acid, $C_4N_2H_4O_5$.—The barium-salt of this acid is deposited in small, colourless, pearly crystals, when baryta-water is added to a solution of alloxan heated to 60°, as long as the precipitate first produced redissolves, and the filtered solution is then left to cool. The barium may be separated by the cautious addition of dilute sulphuric acid, and the filtered liquid, on gentle evaporation, yields alloxanic acid in small radiated needles. It has an acid taste and reaction, decomposes carbonates, and dissolves zinc with disengagement of hydrogen. It is a bibasic acid. The alloxanates of the alkali-metals are freely soluble: those of the earth-metals dissolve in a large quantity of tepid water; that of silver is quite insoluble and anhydrous.

On boiling its salts with water, the alloxanic acid is resolved into urea and mesoxalic acid. The free acid when boiled yields oxalantin.

Dialuric Acid, $C_4H_4N_2O_4$, is the final product of the action of reducing agents on alloxan, and is formed when sulphuretted hydrogen is passed through a boiling solution of alloxan till no further action takes place: $C_4H_2N_2O_4 + H_2S = C_4H_4N_2O_4 + S$. On adding to an aqueous solution of alloxan, first a small quantity of hydrocyanic acid and then potassium carbonate, the potassium salt of dialuric acid separates out in granular crystals, whilst oxalurate remains dissolved:

$$2C_4H_2N_2O_4 + 2KOH = C_4H_3KN_2O_4 + C_3H_3KN_2O_4 + CO_2 .$$

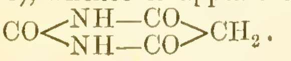
Dialuric acid separated from its salts by hydrochloric acid crystallises in needles, has a strong acid reaction, and when exposed to the air turns red, absorbs oxygen, and is converted into alloxantin:

$$2C_4H_4N_2O_4 + O = 2H_2O + C_8H_4N_4O_7 .$$

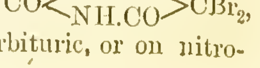
Barbituric Acid, $C_4H_4N_2O_3$, is formed by the action of sodium-amalgam or hydriodic acid on dibromobarbituric acid; also by heating a solution of alloxantin with strong sulphuric acid, barbituric acid then separating out, while parabanic acid remains in solution.

Barbituric acid crystallises in beautiful prisms containing two molecules of water. It is bibasic, and yields chiefly acid salts, which are obtained by treating the corresponding acetates with barbituric acid.

Barbituric acid is converted by fuming nitric acid into dilituric acid; by potassium nitrate into potassium violurate. When boiled with potash it gives off ammonia, and yields the potassium-salt of malonic acid, $C_3H_4O_4$ (p. 343), whence it appears to have the constitution of malonyl-urea,



$$CO\left<\begin{matrix}NH-CO\\NH-CO\end{matrix}\right>CH_2 .$$



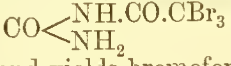
Dibromobarbituric acid, $C_4H_2Br_2N_2O_3 = CO\left<\begin{matrix}NH.CO\\NH.CO\end{matrix}\right>CBr_2$, is formed by the action of bromine on barbituric, or on nitro-

nitroso-, or amido-barbituric acid; also, together with alloxan, by the action of bromine on hydurilic acid:

$$C_8H_6N_4O_6 + Br_6 + H_2O = C_4H_2N_2Br_2O_3 + C_4H_2N_2O_4 + 4HBr.$$

It crystallises in colourless, shining plates, or prisms, soluble in water, very soluble in alcohol and ether. By *hydrogen sulphide*, in presence of water, it is reduced to dialuric acid:

$$C_4H_2N_2Br_2O_3 + H_2S + H_2O = C_4H_4N_2O_4 + 2HBr + S.$$

When chlorine or bromine acts upon a warm solution of dibromobarbituric acid, carbon dioxide is eliminated and tribromacetylurea,  $CO<\begin{matrix}NH.CO.CBr_3\\NH_2\end{matrix}$, is produced. This compound melts at 148°, and yields bromoform when boiled with water.

Monobromobarbituric acid, $C_4H_3BrN_2O_3$, produced by the action of zinc or aqueous hydrocyanic acid on dibromobarbituric acid, forms crystals sparingly soluble in water.

Nitrobarbituric or *Dilituric acid*, $C_4H_3(NO_2)N_2O_3$, is formed by the action of fuming nitric acid on barbituric acid, or of ordinary nitric acid on hydurilic acid. It crystallises in colourless square prisms containing $3H_2O$, soluble in water with yellow colour. It appears to be tribasic, but is most inclined to form salts containing only one equivalent of metal. Its salts are very stable, most of them resisting the action of mineral acids. By heating with bromine, it is converted into dibromobarbituric acid.

Nitrosobarbituric or *Violuric acid*, $C_4H_3(NO)N_2O_3$, is formed by the action of nitric acid of specific gravity 1·2 on hydurilic acid, also by that of potassium nitrite on barbituric acid. The resulting solution is mixed with barium chloride, and the barium salt thereby precipitated is decomposed by sulphuric acid.

Violuric acid crystallises in yellow rhombic octohedrons containing one molecule of H_2O, moderately soluble in water. It forms blue, violet, or yellow salts containing one equivalent of metal. The *potassium salt*, $C_4H_2K(NO)N_2O_3 + 2H_2O$, forms dark blue prisms, dissolving in water with violet colour. The *sodium salt* is dark red. The solution of the acid is coloured dark blue by ferric acetate, and on adding alcohol to the solution, a ferric salt is precipitated in six-sided laminæ having a red colour and metallic lustre.

Violuric acid heated with potash-ley is resolved into urea and nitrosomalonic acid:

$$C_4H_3(NO)N_2O_3 + 2H_2O = CON_2H_4 + C_3H_3(NO)O_4.$$

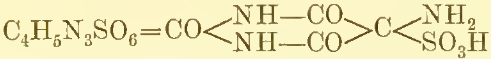
Amidobarbituric acid, $C_4H_3(NH_2)N_2O_3$, also called *Uramil*, *Dialuramide*, and *Murexan*, is formed by the action of hydriodic acid on violuric acid or dilituric acid, or by boiling a solution of ammonium thionurate with hydrochloric acid. It is best prepared by boiling alloxantin with an aqueous solution of sal-ammoniac:

$$\underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + NH_3.HCl = \underset{\text{Uramil.}}{C_4H_3(NH_2)N_2O_3} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + HCl$$

It crystallises in colourless needles, turning red on exposure to the air, nearly insoluble in cold water, slightly soluble in boiling water, easily in alkalis. The ammoniacal solution becomes purple on exposure to the air, and yields murexid on boiling. Uramil is decomposed by strong *nitric acid*, with formation of ammonium nitrate and alloxan:

$$C_4H_5N_3O_3 + O = NH_3 + C_4H_2N_2O_4 .$$

Heated with aqueous *potassium cyanate* it is converted into pseudo-uric acid (p. 411): $C_4H_5N_3O_3 + CNHO = C_5H_6N_4O_4$.—By the action of *mercuric* or *argentic oxide* suspended in boiling water, it is converted into murexid.

Thionuric Acid,  $C_4H_5N_3SO_6 = CO{<}\begin{matrix}NH-CO\\NH-CO\end{matrix}{>}C{<}\begin{matrix}NH_2\\SO_3H\end{matrix}$.—This acid, which contains the elements of alloxan, ammonia, and sulphurous oxide ($C_4H_2N_2O_4 + NH_3 + SO_2$), is formed, as an ammonium-salt, when a cold solution of alloxan is mixed with a saturated aqueous solution of sulphurous acid, in such quantity that the odour of the gas remains quite distinct: an excess of ammonium carbonate mixed with a little caustic ammonia is then added, and the whole boiled for a few minutes. On cooling, *ammonium thionurate* is deposited in colourless, crystalline plates, which, by solution in water and re-crystallisation, acquire a fine pink tint. By converting it into a lead salt, and decomposing the latter with hydrogen sulphide, thionuric acid is obtained as a white crystalline mass, very soluble in water. When its solution is heated to the boiling point, it is resolved into sulphuric acid and uramil:

$$C_4H_5N_3SO_6 + H_2O = H_2SO_4 + C_4H_5N_3O_3 .$$

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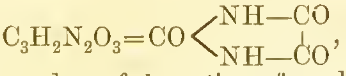
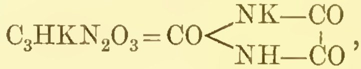
2. *Oxalic Series.*

Parabanic Acid,  $C_3H_2N_2O_3 = CO{<}\begin{matrix}NH-CO\\ \quad\ \ |\\NH-CO\end{matrix}$, *Oxalyl urea.*—This is the characteristic product of the action of moderately strong nitric acid on uric acid or alloxan, *with the aid of heat;* formed also from the same substances by oxidation with manganese dioxide and sulphuric acid:

$$C_5H_4N_4O_3 + O_2 + 2H_2O = C_3H_2N_2O_3 + 2CO_2 + 2NH_3 .$$

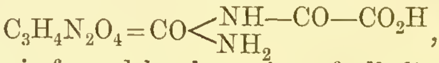
It is conveniently prepared by heating 1 part of uric acid with 8 parts of nitric acid till the reaction has nearly ceased; the liquid is evaporated to a syrup and left to cool; and the product drained from the mother-liquor is purified by recrystallisation. Parabanic acid forms colourless, transparent, thin, prismatic crystals, permanent in the air : it is easily soluble in water, has a pure and powerfully acid taste, and reddens litmus strongly. Neutralised with ammonia, and boiled for a moment, it yields on cooling crystals of the ammonium salt of oxaluric acid, $C_3H_4N_2O_4$, from which the acid may be separated by sulphuric acid.

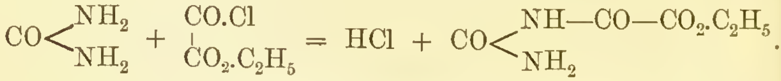
Parabanic acid is bibasic. With the alkali-metals it forms monometallic salts, like  $C_3HKN_2O_3 = CO\begin{array}{l}\diagup NK{-}CO \\ \qquad\quad | \\ \diagdown NH{-}CO\end{array}$, which are obtained as crystalline precipitates on adding potassium- or sodium-ethylate to a solution of parabanic acid in absolute alcohol ; when dissolved in water, these salts are converted into oxalurates. Silver nitrate, added to a solution of the acid, throws down the diargentic salt, $C_3Ag_2N_2O_3$.

Parabanic acid boiled with dilute acids is resolved into urea and oxalic acid. In presence of alkalis, it takes up water, and is converted into oxaluric acid, $C_3H_4N_2O_4$. By the action of zinc and hydrochloric acid, it is converted into oxalantin, $C_6H_4N_4O_5 = 2C_3H_2N_2O_3 - O$.

Methyl-parabanic acid, $C_3H(CH_3)N_2O_3$, is obtained by decomposition of creatinine.

Dimethyl-parabanic acid or *Cholestrophane,* $C_3(CH_3)_2N_2O_3$, obtained by heating the silver salt of parabanic acid with methyl iodide, forms silvery laminæ, which easily melt and sublime.

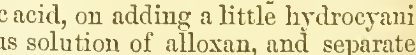
Oxaluric Acid,  $C_3H_4N_2O_4 = CO\begin{array}{l}\diagup NH{-}CO{-}CO_2H \\ \diagdown NH_2\end{array}$, the analogue of alloxanic acid, is formed by the action of alkalis on parabanic acid. Its ethylic ether is produced by heating urea with chloroxalic ether:

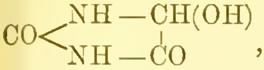


$$CO\begin{array}{l}\diagup NH_2 \\ \diagdown NH_2\end{array} + \begin{array}{l}CO.Cl \\ | \\ CO_2.C_2H_5\end{array} = HCl + CO\begin{array}{l}\diagup NH{-}CO{-}CO_2.C_2H_5 \\ \diagdown NH_2\end{array}.$$

It crystallises in silky needles, which melt with decomposition at 150°-160°.

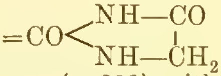
Oxaluric acid, separated from its salts by a mineral acid, is a heavy crystalline powder. Its salts are sparingly soluble. Boiled with water or alkalis, it is resolved into oxalic acid and urea. Heated to 200° with phosphorus trichloride, it gives up water, and is reconverted into parabanic acid.

Oxaluramide or **Oxalan,**  $C_3H_5N_3O_3 = CO\begin{array}{l}\diagup NH.CO.CO.NH_2 \\ \diagdown NH_2\end{array}$, is formed, together with dialuric acid, on adding a little hydrocyanic acid and ammonia to an aqueous solution of alloxan, and separates as a white precipitate, while the dialuric acid remains dissolved. It is also produced by heating ammonium parabanate (its isomeride) to 100°, and by heating ethyloxalurate with ammonia. It is sparingly soluble in water and is resolved by boiling with water, into oxalic acid, urea, and ammonia.

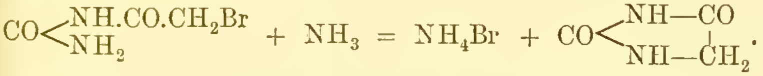


Allanturic Acid or **Oxyglycolyl-urea,** $C_3H_4N_2O_3 = \mathrm{CO}<\begin{array}{l}\mathrm{NH-CH(OH)}\\ \qquad\quad | \\ \mathrm{NH-CO}\end{array}$, formed by heating allantoin with baryta-water or dioxide of lead, is a deliquescent mass, the aqueous solution of which gives white precipitates with silver or lead salts. When boiled with baryta, it yields hydantoic and parabanic acids, the latter further splitting up into oxaluric acid and urea (or CO_2 and NH_3).

Succinuric Acid, $C_5H_8N_2O_4$, is produced by heating urea to 120°–130° with succinic anhydride. It forms shining scales, melting with decomposition at 203°–205°.



Hydantoin or **Glycolyl-urea,** $C_3H_4N_2O_2 = \mathrm{CO}<\begin{array}{l}\mathrm{NH-CO}\\ \qquad\ | \\ \mathrm{NH-CH_2}\end{array}$ is formed synthetically by heating bromacetyl-urea (p. 398) with alcoholic ammonia:

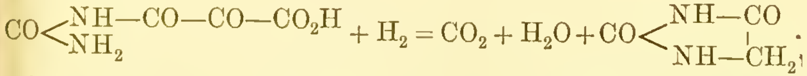


$$\mathrm{CO}<\begin{array}{l}\mathrm{NH.CO.CH_2Br}\\ \mathrm{NH_2}\end{array} + NH_3 = NH_4Br + \mathrm{CO}<\begin{array}{l}\mathrm{NH-CO}\\ \qquad\ | \\ \mathrm{NH-CH_2}\end{array}.$$

It is also produced by the action of hydriodic acid on allantoin:

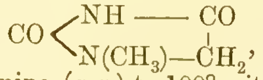
$$C_4H_6N_4O_3 + 2HI = C_3H_4N_2O_2 + CON_2H_4 + I_2,$$

or on alloxanic acid:

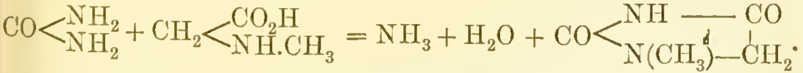


$$\mathrm{CO}<\begin{array}{l}\mathrm{NH-CO-CO-CO_2H}\\ \mathrm{NH_2}\end{array} + H_2 = CO_2 + H_2O + \mathrm{CO}<\begin{array}{l}\mathrm{NH-CO}\\ \qquad\ | \\ \mathrm{NH-CH_2}\end{array}.$$

Hydantoin forms needle-shaped crystals, having a faint sweet taste, and melting at 206°. When boiled with baryta-water, it takes up water and is converted into hydantoic acid.

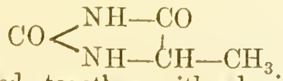


Methyl-hydantoin, $\mathrm{CO}<\begin{array}{l}\mathrm{NH\ —\ CO}\\ \qquad\qquad | \\ \mathrm{N(CH_3)-CH_2}\end{array}$, is obtained by prolonged heating of creatinine (*q.v.*) to 100° with baryta-water; also by fusing urea with sarcosine (methyl-glycocine):



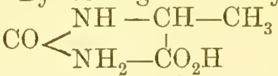
$$\mathrm{CO}<\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH_2}\end{array} + \mathrm{CH_2}<\begin{array}{l}\mathrm{CO_2H}\\ \mathrm{NH.CH_3}\end{array} = NH_3 + H_2O + \mathrm{CO}<\begin{array}{l}\mathrm{NH\ —\ CO}\\ \qquad\qquad | \\ \mathrm{N(CH_3)-CH_2}\end{array}.$$

It forms crystals easily soluble in water and in alcohol, melts at 145°, and sublimes in shining needles. Boiled with oxide of mercury or silver it yields metallic derivatives.



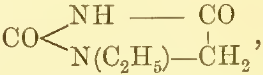
Lactyl-urea, $\mathrm{CO}<\begin{array}{l}\mathrm{NH-CO}\\ \qquad\ | \\ \mathrm{NH-CH-CH_3}\end{array}$ metameric with methyl-hydantoïn, is formed, together with alanine, when the potassium cyanide used in the preparation of the latter from aldehyde-ammonia

(p. 381) contains cyanate. It forms efflorescent rhombic crystals, containing $C_4H_6N_2O_2+H_2O$; melts at 140°, and sublimes with partial decomposition. By boiling with baryta-water it is converted into lacturic acid,



$\mathrm{CO}<\begin{matrix}\mathrm{NH-CH-CH_3}\\ \mathrm{NH_2-CO_2H}\end{matrix}$, metameric with methyl-hydantoic acid, which melts at 155°.

Ethyl-hydantoïn,



$\mathrm{CO}<\begin{matrix}\mathrm{NH \text{——} CO}\\ \mathrm{N(C_2H_5)-CH_2}\end{matrix}$, produced in like manner by melting urea with ethyl-glycocine, crystallises in large, flat prisms, easily soluble in water and alcohol, melting at about 100°, and easily subliming.

The metameric compound, acetonyl-urea, $\mathrm{CO}<\begin{matrix}\mathrm{NH-C(CH_3)_2}\\ \mathrm{NH-CO}\end{matrix}$, formed by heating a mixture of acetone and potassium cyanide containing cyanate with fuming hydrochloroic acid, crystallises in prisms, melting at 175°. By boiling with baryta-water it is converted into acetonuric acid, $C_5H_{10}N_2O_3$.

Hydantoic or **Glycoluric Acid**, $C_3H_6N_2O_3 = \mathrm{CO}<\begin{matrix}\mathrm{NH-CH_2-CO_2H}\\ \mathrm{NH_2}\end{matrix}$, is produced by boiling allantoin, hydantoin, or glycoluril with baryta-water, and synthetically by heating glycocine with urea (or by boiling its solution with baryta-water :)

$$\mathrm{CO}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix} + \mathrm{CH_2}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{CO_2H}\end{matrix} = \mathrm{NH_3} + \mathrm{CO}<\begin{matrix}\mathrm{NH-CH_2-CO_2H}\\ \mathrm{NH_2}\end{matrix};$$

also by heating glycocine sulphate with potassium cyanate :

$$\mathrm{CO{=}NH} + \mathrm{CH_2}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{CO_2H}\end{matrix} = \mathrm{CO}<\begin{matrix}\mathrm{NH-CH_2-CO_2H}\\ \mathrm{NH_2}\end{matrix}.$$

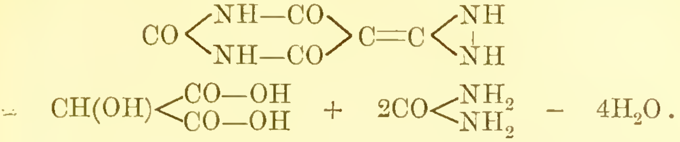
Hydantoic acid forms large rhombic prisms soluble in water. It is monobasic, and most of its salts are easily soluble. By heating with hydriodic acid it is converted into glycocine:

$$\mathrm{CO}<\begin{matrix}\mathrm{NH-CH_2-CO_2H}\\ \mathrm{NH_2}\end{matrix} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{CH_2}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{CO_2H}\end{matrix}.$$

Diureides.

The best known compounds of this class contain 4, 5, 6, or 8 atoms of carbon. The 4- and 5- carbon diureides (including uric acid itself) are formed by the union of one molecule of a bibasic acid and 2 molecules of urea, with elimination of 4 molecules of water, and accordingly contain one diatomic acid residue and two urea-residues, $\mathrm{CO}<\begin{matrix}\mathrm{NH}\\ \mathrm{NH}\end{matrix}$.

Uric Acid, $C_5H_4N_4O_3$, as already observed, may be regarded as the diureide of tartronic acid, and accordingly represented by the formula:

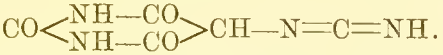


$$CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>C=C<\begin{array}{l}NH\\|\\NH\end{array}$$

$$= CH(OH)<\begin{array}{l}CO-OH\\CO-OH\end{array} + 2CO<\begin{array}{l}NH_2\\NH_2\end{array} - 4H_2O.$$

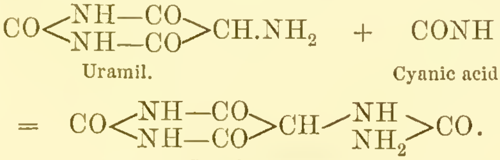
Tartronic acid. Urea.

Iso-uric Acid, $C_5H_4N_4O_3$, is formed by the action of cyanamide on alloxantin in aqueous solution, and separates on boiling in the form of a heavy powder. Its constitution may perhaps be represented by the formula:



$$CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>CH-N=C=NH.$$

Pseudo-uric Acid, $C_5H_6N_4O_4$.—The potassium salt of this acid is obtained as a yellow crystalline powder by boiling uramil with a strong solution of potassium cyanate. The free acid forms colourless crystals, slightly soluble in water. Its structure and formation may be represented as follows:



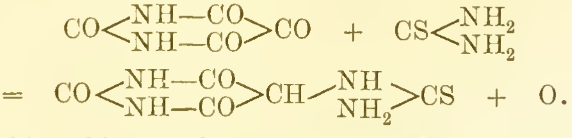
$$CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>CH.NH_2 + CONH$$

Uramil. Cyanic acid.

$$= CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>CH-\begin{array}{l}NH\\NH_2\end{array}>CO.$$

Pseudo-uric acid.

Pseudo-thiouric Acid, $C_5H_6N_4O_3S$, is formed by heating alloxan and thiocarbamide with a concentrated alcoholic solution of sulphur dioxide:



$$CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>CO + CS<\begin{array}{l}NH_2\\NH_2\end{array}$$

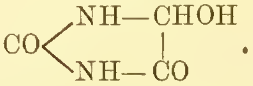
$$= CO<\begin{array}{l}NH-CO\\NH-CO\end{array}>CH-\begin{array}{l}NH\\NH_2\end{array}>CS + O.$$

It forms thin white needles, insoluble in water, but soluble in acids.

Uroxanic Acid, $C_5H_8N_4O_6$, and **Oxonic Acid,** $C_4H_5N_3O_4$.—These acids are formed by gradual oxidation of uric acid in alkaline solution. A solution of uric acid in potash left for some time in an open vessel deposits shining laminæ of potassium uroxanate, $C_5H_6K_2N_4O_6 + 3H_2O$, from which the free acid may be separated by hydrochloric acid in the form of a crystalline powder, which dissolves in hot water, but decomposes at the same time, with separation of carbon dioxide. Its formation is represented by the equation:

$$C_5H_4N_4O_3 + 2H_2O + O = C_5H_8N_4O_6.$$

Potassium uroxanate, at the moment of its formation, is partly converted, by separation of CO_2 and NH_3, into potassium oxonate, $C_4H_3K_2N_3O_4$, which is also formed by passing a stream of air through a solution of uric acid in potash till all the uric acid is oxidised. This salt forms radiate groups of crystals, containing 1½ mol. H_2O. Acetic acid added to its dilute solution throws down the potassium salt of allanturic acid, or oxyglycolyl-urea, $C_3H_4N_2O_3$ or



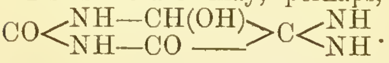
$$CO<\begin{array}{l}NH-CHOH\\ \qquad\quad |\\ NH-CO\end{array} .$$

Allantoin, $C_4H_6N_4O_3$.—This substance, which contains the elements of 2 molecules of ammonium oxalate minus 5 molecules of water $[2C_2(NH_4)_2O_4-5H_2O]$, is found in the allantoïc liquid of the fœtal calf and in the urine of the sucking calf. It is produced artificially, together with oxalic acid and urea, by boiling uric acid with lead dioxide and water:

$$2C_5H_4N_4O_3 + O_6 + 5H_2O = C_4H_6N_4O_3 + 2C_2H_2O_4 + 2CH_4N_2O_3.$$

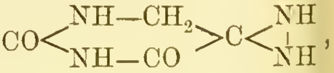
The liquid filtered from lead oxalate, and concentrated by evaporation, deposits, on cooling, crystals of allantoïn, which are purified by re-solution and the use of animal charcoal. The mother-liquor, when further concentrated, yields crystals of pure urea. Allantoïn forms small but brilliant prismatic crystals, transparent, colourless, tasteless, and without action on vegetable colours. It dissolves in 160 parts of cold water, and in a smaller quantity at the boiling heat. It is decomposed by boiling with nitric acid, and by oil of vitriol when concentrated and hot, into ammonia, carbon dioxide, and carbon monoxide. Heated with concentrated solutions of caustic alkalis, it is decomposed into ammonia and oxalic acid.

Its structure may, perhaps, be represented by the formula



$$CO<\begin{array}{l}NH-CH(OH)\\ NH-CO \text{ ——}\end{array}>C<\begin{array}{l}NH\\ NH\end{array}.$$

Glycoluril, $C_4H_6N_4O_2$, probably

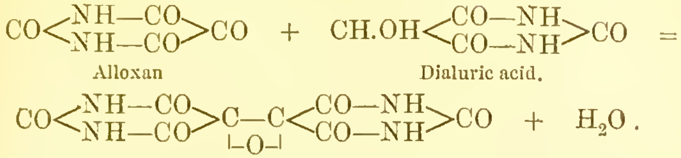


$$CO<\begin{array}{l}NH-CH_2\\ NH-CO\end{array}>C<\begin{array}{l}NH\\ \ |\\ NH\end{array},$$

is formed by the action of sodium amalgam on allantoïn, and separates in octohedral crystals, sparingly soluble in water, moderately soluble in ammonia and in concentrated acids. Ammoniacal silver nitrate forms in its solutions a yellow precipitate having the composition $C_4H_4Ag_2N_4O_2$. By boiling with baryta-water it is resolved into urea and hydantoic acid, and by boiling with acids it is converted into hydantoïn.

Diureides containing 6 and 8 atoms of carbon are formed by the union of 2 monureide molecules, with elimination of water.

Alloxantin, $C_8H_4N_4O_7$, is formed on mixing the aqueous solutions of alloxan and dialuric acid :



$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}>\mathrm{CO} \quad + \quad \mathrm{CH.OH}<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO{-}NH}\end{matrix}>\mathrm{CO} \quad =$$

Alloxan Dialuric acid.

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}>\underset{|\!-\mathrm{O}-\!|}{\mathrm{C{-}C}}<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO{-}NH}\end{matrix}>\mathrm{CO} \quad + \quad H_2O\,.$$

Alloxantin.

It is the chief product of the action of hot dilute nitric acid upon uric acid, and is likewise produced by the action of deoxidising agents upon alloxan,—anhydrous alloxantin, in fact, containing 1 atom of oxygen less than 2 molecules of alloxan. It is best prepared by passing sulphuretted hydrogen gas through a moderately strong and cold solution of alloxan. The mother-liquor from which the crystals of alloxan have separated answers the purpose perfectly well ; it is diluted with a little water, and a copious stream of gas transmitted through it. Sulphur is then deposited in large quantity, mixed with a white, crystalline substance, which is the alloxantin. The product is drained upon a filter, slightly washed, and then boiled in water : the filtered solution deposits the alloxantin on cooling. Alloxantin forms small, four-sided, oblique rhombic prisms, colourless and transparent ; it dissolves with difficulty in cold water, but more freely at the boiling heat. The solution reddens litmus, gives with baryta-water a violet-coloured precipitate, which disappears on heating, and when mixed with silver nitrate produces a black precipitate of metallic silver. Heated with chlorine or nitric acid, it is oxidised to alloxan. The crystals become red when exposed to ammoniacal vapours. They contain 3 mol. H_2O, which they do not give off till heated above 150°.

Alloxantin is readily decomposed ; when a stream of sulphuretted hydrogen is passed through its boiling solution, sulphur is deposited and dialuric acid is produced. A hot saturated solution of alloxantin mixed with a neutral salt of ammonia instantly assumes a purple colour, which, however, quickly vanishes, the liquid becoming turbid from formation of uramile : the solution then contains alloxan and free acid. With silver oxide, alloxantin gives off carbon dioxide, reduces a portion of the metal, and converts the remainder of the oxide into oxalurate. Boiled with water and lead dioxide, it gives urea and lead carbonate.

Hydurilic Acid, $C_8H_6N_4O_6$.—Dialuric acid, heated to about 160° with glycerin (which acts merely as a solvent), splits up into formic acid, carbon dioxide, and ammonium hydurilate :

$$5C_4H_4N_2O_4 = CH_2O_2 + 3CO_2 + 2C_8H_5N_4(NH_4)O_6\,.$$

By converting this ammonium-salt into a copper-salt, and decomposing the latter with H_2S, hydurilic acid is obtained in crystals.

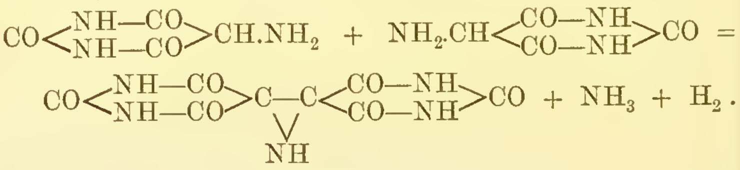
Hydurilic acid is converted by fuming nitric acid into alloxan, without any other product; but with nitric acid of ordinary strength it yields alloxan, together with violuric acid, violantin, and dilituric acid:

$$\underset{\text{Hydurilic acid.}}{C_8H_6N_4O_6} + NO_3H = \underset{\text{Violuric acid.}}{C_4H_3N_3O_4} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + H_2O$$

$$\underset{\text{Hydurilic acid.}}{C_8H_6N_4O_6} + 2NO_3H = \underset{\text{Dilituric acid.}}{C_4H_3N_3O_5} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + NO_2H + H_2O.$$

If the action be carried on to the end, dilituric acid is the only product. This acid may indeed be regarded as a product of the oxidation of violuric acid: $C_4N_3H_3O_5 = C_4N_3H_3O_4 + O$: and violantin as a compound of the two.

Purpuric Acid, $C_8H_5N_5O_6$, is not known in the free state; its ammonium salt, $C_8H_4(NH_4)N_5O_6$, constitutes murexid. This salt contains the elements of two molecules of uramil minus two atoms of hydrogen:



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}\right>\mathrm{CH.NH_2} + \mathrm{NH_2.CH}\left<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO{-}NH}\end{matrix}\right>\mathrm{CO} =$$

$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH{-}CO}\end{matrix}\right>\mathrm{C}\underset{\mathrm{NH}}{\underset{\vee}{-}}\mathrm{C}\left<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO{-}NH}\end{matrix}\right>\mathrm{CO} + \mathrm{NH_3} + \mathrm{H_2}.$$

Purpuric acid.

It is formed by mixing the ammoniacal solutions of alloxan and uramil:

$$C_4H_2N_2O_4 + C_4H_5N_3O_3 + NH_3 = H_2O + C_8H_4(NH_4)N_5O_6,$$

and is best prepared by boiling for a few minutes a mixture of 1 part of dry uramil, 1 part of mercuric oxide, and 40 parts of water rendered slightly alkaline by ammonia:

$$2C_4H_5N_3O_3 + O = H_2O + C_8H_8N_6O_6.$$

Another method is that of Dr. Gregory: 7 parts of alloxan and 4 parts of alloxantin are dissolved in 240 parts of boiling water, and the solution is added to about 80 parts of cold strong solution of ammonium carbonate: the liquid instantly acquires such a depth of colour as to become opaque, and gives on cooling a large quantity of murexide: the operation succeeds best on a small scale.

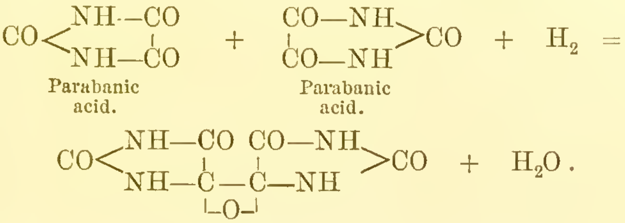
Murexid* crystallises with 1 molecule H_2O in small square plates or prisms, which by reflected light exhibit a splendid green metallic lustre, like that of the wing-cases of the rose-beetle and other insects: by transmitted light they are deep purple-red. It dissolves with difficulty in cold water, much more easily at the boiling heat, but is insoluble in alcohol and ether. Mineral acids decompose it, with separation of a white or yellowish substance called murexan, probably identical with uramil. Caustic potash dissolves it, with production of a magnificent purple colour, which disappears on boiling.

---

* So called from the Tyrian dye, said to have been prepared from a species of *murex*.

A few years ago murexid was extensively used in dyeing; but it is now to a great extent superseded by rosaniline.

Oxalantin, $C_6H_4N_4O_5$, also called *leucoturic acid,* is formed by the action of zinc and hydrochloric acid on parabanic acid:



$$CO<\begin{matrix}NH-CO\\ \quad\ \ |\\ NH-CO\end{matrix} + \begin{matrix}CO-NH\\ |\quad\quad\\ CO-NH\end{matrix}>CO + H_2 =$$

Parabanic acid. Parabanic acid.

$$CO<\begin{matrix}NH-CO & CO-NH\\ \quad\ \ | & |\quad\quad\\ NH-C & -C-NH\\ \quad\ \ \llcorner & -O-\lrcorner\end{matrix}>CO + H_2O.$$

Oxalantin.

It forms small crystals slightly soluble in water, and reduces ammoniacal solutions of mercury and silver.

Alliturie Acid, $C_6H_6N_4O_4$, is formed, together with alloxan and parabanic acid, by boiling alloxantin with hydrochloric acid. It forms crystals sparingly soluble in water, and when heated with water to 180°–190°, is resolved into oxalic acid, carbon dioxide and monoxide, and ammonia.

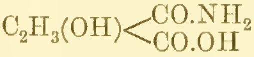
Respecting basic compounds, natural and artificial, related to the ureides by their composition and reactions, see ALKALOIDS.

AMIDES DERIVED FROM TRIATOMIC AND TETRATOMIC ACIDS.

Our knowledge of these amides is somewhat limited: we shall notice only those derived from malic, tartaric, and citric acids:

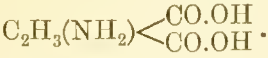
1. Amides of Malic Acid.

Malic acid, $CO_2H-CH_2-CHOH-CO_2H$, or $C_2H_3(OH)<\begin{matrix}CO_2H\\ CO_2H\end{matrix}$, which is triatomic and bibasic, is capable of yielding five amides, viz.:



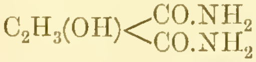
$$C_2H_3(OH)<\begin{matrix}CO.NH_2\\ CO.OH\end{matrix}$$

Malamic acid.



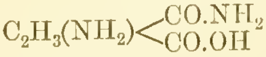
$$C_2H_3(NH_2)<\begin{matrix}CO.OH\\ CO.OH\end{matrix}.$$

Aspartic acid.



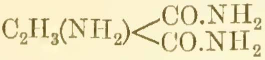
$$C_2H_3(OH)<\begin{matrix}CO.NH_2\\ CO.NH_2\end{matrix}$$

Malamide.



$$C_2H_3(NH_2)<\begin{matrix}CO.NH_2\\ CO.OH\end{matrix}$$

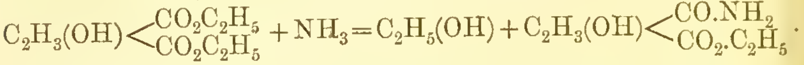
Asparagin.



$$C_2H_3(NH_2)<\begin{matrix}CO.NH_2\\ CO.NH_2\end{matrix}$$

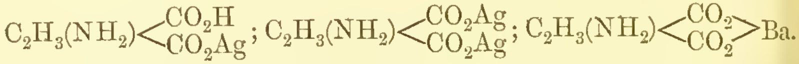
Triamide (unknown).

Malamic acid is not known in the free state, but its ethylic ether, or *Malamethane*, $C_2H_3(OH)<\begin{matrix}CO.NH_2\\CO.C_2H_5\end{matrix}$, is formed as a crystalline mass when ammonia gas is passed into an alcoholic solution of diethylic malate:



$$C_2H_3(OH)<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix} + NH_3 = C_2H_5(OH) + C_2H_3(OH)<\begin{matrix}CO.NH_2\\CO_2.C_2H_5\end{matrix}.$$

Aspartic acid, $C_4H_7NO_4$, isomeric with malamic acid, is related to malic and succinic acids in the same manner as glycocine to glycollic and acetic acids (p. 380), and may accordingly be regarded as amidosuccinic acid. It occurs in beet-molasses, and is produced by various reactions from albuminous substances. It is prepared by boiling asparagin with alkalis or acids. It crystallises in small rhombic prisms, moderately soluble in hot water. Its alkaline solutions turn the plane of polarisation to the left; acid solutions to the right. Like other amido-acids, it unites both with acids and with alkalis; with the latter it forms both acid and neutral salts; *e.g.*,



$$C_2H_3(NH_2)<\begin{matrix}CO_2H\\CO_2Ag\end{matrix};\ C_2H_3(NH_2)<\begin{matrix}CO_2Ag\\CO_2Ag\end{matrix};\ C_2H_3(NH_2)<\begin{matrix}CO_2\\CO_2\end{matrix}>Ba.$$

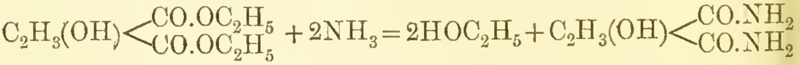
By the action of nitrous acid it is converted into malic acid.

An inactive aspartic acid is obtained by heating fumarimide with water:

$$C_4H_2O_2.NH + 2H_2O = C_4H_7NO_4.$$

It crystallises in large monoclinic prisms, somewhat more soluble in water than the optically active acid. By nitrous acid it is converted into inactive malic acid.

Malamide, $C_4H_8N_2O_3$, is produced by the action of ammonia in excess on dry diethylic malate:



$$C_2H_3(OH)<\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix} + 2NH_3 = 2HOC_2H_5 + C_2H_3(OH)<\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}$$

It forms large crystals, and when heated with water is resolved into ammonia and malic acid.

Asparagin, $C_2H_3(NH_2)<\begin{matrix}CO.NH_2\\CO.OH\end{matrix}$, isomeric with malamide, occurs in numerous plants, as asparagus, marsh mallow, mangold-wurzel, peas, beans, vetches, and cereal grasses, especially in the young sprouts. It may be prepared from marsh-mallow roots by chopping them small, macerating them in the cold with milk of lime, precipitating the filtered liquid with barium carbonate, and evaporating the clear solution over the water-bath to a syrup. The asparagin then crystallises on cooling in shining transparent rhombic prisms, which have a faint cooling taste, and are moderately soluble in hot water, insoluble in alcohol and in ether. The crystals contain one molecule of water, whereas those of malamide are anhydrous.

Asparagin and malamide differ also in their action on polarised light, malamide having a specific rotatory power of $-47{\cdot}5°$, whereas that of asparagin in an acid solution is $+35°$, and in an ammoniacal solution $-11° 18'$. Lastly, malamide, when treated with alkalis is resolved, as already observed, into ammonia and malic acid, whereas asparagin yields ammonia and aspartic acid.

Asparagin forms salts both with acids and with bases.

By fermentation in contact with albuminous substances, asparagin is converted into ammonium succinate. By oxidation with potassium permanganate it yields ammonium formate, hydrocyanic acid, and carbon dioxide :

$$C_4H_8N_2O_3 + O_4 = CHO_2.NH_4 + CNH + 2CO_2 + H_2O\,.$$

In presence of sulphuric acid the oxidation takes place according to the equation,

$$C_4H_8N_2O_3 + O_6 = 2NH_3 + 4CO_2 + H_2O\,;$$

in presence of potash the products are ammonia and oxalic acid :

$$C_4H_8N_2O_3 + O_4 + 4KHO = 2NH_3 + 2C_2O_4K_2 + 3H_2O\,.$$

2. **Amides of Tartaric Acid.**—*Tartramic Acid*, $C_4H_7NO_5 = C_2H_2(OH)_2{<}\begin{matrix}CO.NH_2\\CO.OH\end{matrix}$, is obtained as an ammonium-salt by the action of ammonia on tartaric anhydride, $C_4H_4O_5$.

Ethyl tartramate, *Tartramic ether*, or *Tartramethane*, is obtained by the action of alcoholic ammonia on diethylic tartrate. When cautiously heated with alkalis, it yields tartramic acid. Ammonia converts it into tartramide.

Tartramide, $C_4H_8N_2O_4 = C_2H_2(OH)_2{<}\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}$, formed also by the action of ammonia on diethylic tartrate, is a crystalline substance, the solution of which exhibits dextro- or levo-rotation according to the kind of tartaric acid from which it has been prepared.

3. **Citramide,** $C_6H_{11}N_3O_4 = C_3H_4(OH)(CO.NH_2)_3$, obtained by the action of alcoholic ammonia on ethyl or methyl citrate, is a crystalline substance slightly soluble in water.

Citramic acid and citrimide are not known, but phenylic derivatives of these amides have been obtained.

Benzene-Derivatives or Aromatic Group.

The hydrocarbons, C_nH_{2n-6}, viz., benzene and its homologues, together with the alcohols, acids, and bases derived from them, form a group resembling the fatty bodies in many of their chemical relations, but nevertheless exhibiting decided peculiarities, which mark them as a natural family. They are called aromatic, on account of the peculiar and fragrant odours possessed by some of them, especially by certain derivatives of benzene, such as benzoic acid, bitter almond oil, &c.

Intimately related to these bodies are certain other hydrocarbons with their derivatives, containing proportionally smaller numbers of hydrogen-atoms, namely cinnamene C_8H_8, naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, pyrene $C_{16}H_{10}$, and chrysene $C_{18}H_{12}$; and the terpenes, $C_{10}H_{16}$, which contain a larger number of hydrogen-atoms than benzene and its homologues.

HYDROCARBONS, C_nH_{2n-6}.

This is the principal series of the aromatic group, analogous to the paraffin series in the fatty group. The known hydrocarbons belonging to it are represented by the formulæ,

$$C_6H_6,\ C_7H_8,\ C_8H_{10},\ C_9H_{12},\ C_{10}H_{14},\ C_{11}H_{16},\ C_{12}H_{18},\ C_{13}H_{20}.$$

The first is called benzene; the second toluene;* the others admit of isomeric modifications, the names of which will be given hereafter. Many of these hydrocarbons are found in the lighter part of the oil or naphtha obtained by the destructive distillation of coal, and may be separated from one another by fractional distillation.

These hydrocarbons might be regarded as derived from the paraffins by abstraction of 8 atoms of hydrogen (*e.g.*, $C_6H_6 = C_6H_{14} - H_8$), or from the olefines by abstraction of 6 atoms of hydrogen, &c., and accordingly they might be expected to act as octovalent, sexvalent, quadrivalent, or bivalent radicles; and in fact, benzene does form definite compounds with 6 atoms of chlorine and of bromine. But in nearly all cases the aromatic hydrocarbons react as saturated molecules, like the paraffins, yielding, when treated with chlorine, bromine, or nitric acid, not additive compounds, but substitution-products.

Benzene may be represented as a saturated molecule by the following constitutional formula, in which the carbon-atoms are united together by one or two combining units alternately:

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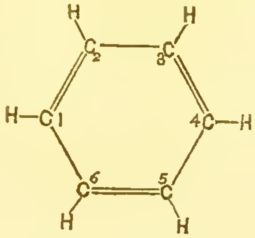
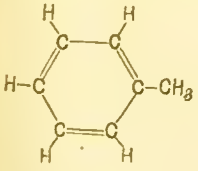
* Frequently also benz*ol*, tolu*ol*, &c.; but it is not desirable to apply the same termination to hydrocarbons and their alcoholic derivatives.



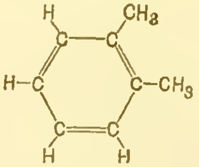
The other hydrocarbons of the series may be derived from it by successive additions of CH_2, or by substitution of methyl, CH_3, in the place of one or more of the hydrogen-atoms; thus:

$C_7H_8 = C_6H_5(CH_3)$ Methyl-benzene.
$C_8H_{10} = C_6H_4(CH_3)_2$ Dimethyl-benzene.
$C_9H_2 = C_6H_3(CH_3)_3$ Trimethyl-benzene.
$C_{10}H_{14} = C_6H_2(CH_3)_4$ Tetramethyl-benzene.

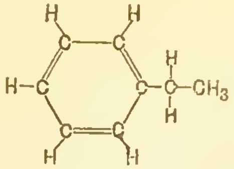
Further, a hydrocarbon isomeric with dimethyl-benzene may be formed by the substitution of ethyl, C_2H_5, for 1 atom of hydrogen in benzene, viz., ethyl-benzene, $C_6H_5(C_2H_5)$; in like manner methyl-ethyl-benzene, $C_6H_4(CH_3)(C_2H_5)$, and propyl-benzene, $C_6H_5(C_3H_7)$, are isomeric with trimethyl-benzene; diethyl-benzene with tetramethyl-benzene, &c., &c. It is easy to see that in this manner a large number of isomeric bodies may exist in the higher terms of the series. The structure of these isomeric hydrocarbons may be illustrated by the following figures:—



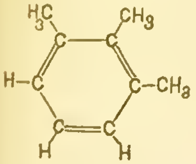
Methyl-benzene.



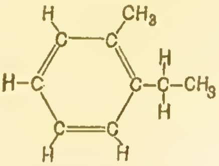
Dimethyl-benzene.



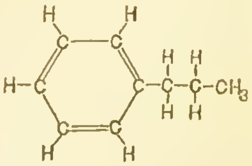
Ethyl-benzene.



Trimethyl-benzene.



Methyl-ethyl-benzene.



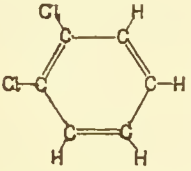
Propyl-benzene.

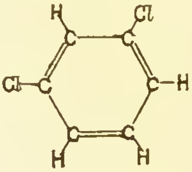
In these homologues of benzene, the six carbon-atoms belonging to the benzene itself are said to form the benzene ring, benzene-nucleus, or principal chain, while the groups CH_3, CH_2CH_3, &c., joined on to these carbon-atoms are called lateral chains. The chemical properties of an aromatic hydrocarbon differ considerably according to the number of lateral chains which it contains.

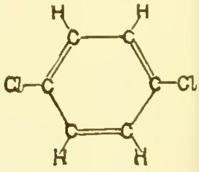
The replacement of the hydrogen-atoms in the principal and lateral chains by Cl, Br, NO_2, OH, NH_2, &c., gives rise to substitution-derivatives which exhibit numerous cases of isomerism.

I. In *Benzene-derivatives.*—The mono-derivatives of benzene do not exhibit isomeric modifications: thus there is but one monobromo-, mononitro-, or mono-amidobenzene, one monohydroxyl-derivative or phenol, $C_6H_5(OH)$, &c. Hence it must be inferred that the molecule of benzene is perfectly symmetrical, all its six carbon-atoms and all its six hydrogen-atoms being equal to one another in value, and discharging similar functions, so that the replacement of a single hydrogen-atom by another element or radicle produces the same effect, in whatever part of the molecule the substitution takes place.

The higher derivatives, on the other hand, formed by replacement of two or more hydrogen-atoms in the molecule, exhibit isomeric modifications which are supposed to depend upon the relative positions, or orientation, of the substituted radicles. Referring to the figure on page 419, in which the carbon-atoms in benzene are numbered from one to six, it is easy to see that there may be three such modifications of dichlorobenzene, $C_6H_4Cl_2$, represented by the following figures :







These three modifications are distinguished by the symbols

1 : 2 1 : 3 1 : 4 .

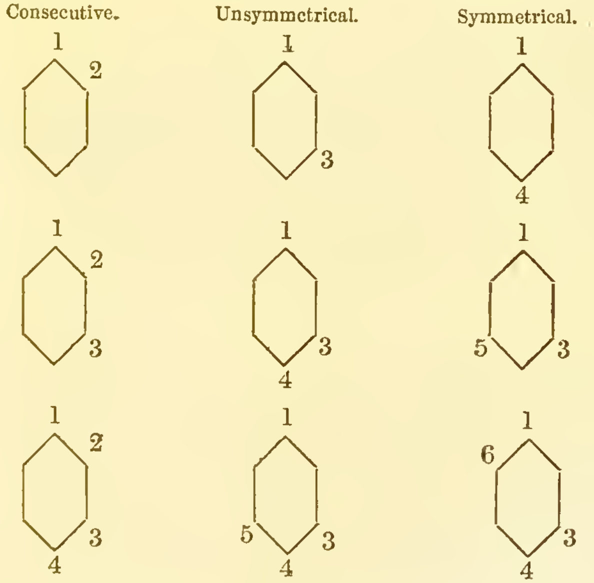
In the first the two chlorine-atoms are contiguous; in the second they are separated by one atom; and in the third by two atoms of hydrogen. It is clear that these are the only three modifications possible : for 2 : 3, 3 : 4, 4 : 5, and 6 : 1, would be the same as 1 : 2; 2 : 4 and 3 : 5 would be the same as 1 : 3; and 2 : 5 and 3 : 6 would be the same as 1 : 4.

The number of possible modifications formed by successive replacement of the hydrogen-atoms in benzene is as follows :

A. *The hydrogen-atoms are successively replaced by the same element or compound radicle.* In this case the number of modifications is as follows :

Number of Hydrogen-atoms replaced.	Number of Modifications.	Positions of the replaced Hydrogen-atoms.		
one	one	1		
two	three	1, 2	1, 3	1, 4
three	three	1, 2, 3	1, 3, 4	1, 3, 5
four	three	1, 2, 3, 4	1, 3, 4, 5	1, 3, 4, 6
five	one	1, 2, 3, 4, 5		
six	one			
		Consecutive.	Unsymmetrical.	Symmetrical.

The meaning of the terms consecutive, symmetrical, and unsymmetrical, applied to the three modifications of the di-, tri-, and tetraderivatives, will be better understood by means of the following diagram :



By counting from different points of the hexagons, it is easy to see that :

in the tri-derivatives, 1,3,4 is the same as 1,2,4, 1,2,5 and 1,3,6
in the tetra-derivatives, 1,3,4,5 ,, 1,2,3,5, 1,2,4,6 and 1,3,5,6
and 1,3,4,6 ,, 1,2,4,5.

B. *The hydrogen-atoms are replaced by different elements or radicles.*

If only two hydrogen-atoms are thus replaced, the number of possible modifications remains the same as above, viz., three ; for the reversal of the order (AB or BA) can make no difference in the result ; but if three or more hydrogen-atoms are replaced by different radicles, the number of possible modifications becomes larger, inasmuch as the order of succession of the substituted radicles may then exert an influence on the nature of the product; thus: to one tribromobenzene, $C_6BrBrBrH_3$, in which the bromine-atoms occupy the places 1, 2, 3, there will correspond two dibromochlorobenzenes, viz., $C_6BrBrClH_3$ and $C_6BrClBrH_3$.

In the present state of our knowledge we cannot in all cases assign to the several radicles which replace the hydrogen in benzene their exact relative positions in each isomeric modification; though so far as regards those derivatives in which the substituted radicles are all alike, the list is nearly complete; but inasmuch as a given modification of a benzene-derivative may in many cases be converted into a particular modification of another benzene-derivative, by simple transformations not likely to be attended by any change of molecular structure, we may conclude that in the two derivatives thus producible one from the other, the radicles which replace two or more atoms of hydrogen will occupy corresponding places. Accordingly, the derivatives of benzene containing a given number of replaced hydrogen-atoms may be divided into groups, each containing those modifications which can be formed one from the other, and in which therefore the radicles which have replaced the hydrogen-atoms may be supposed to be similarly situated.

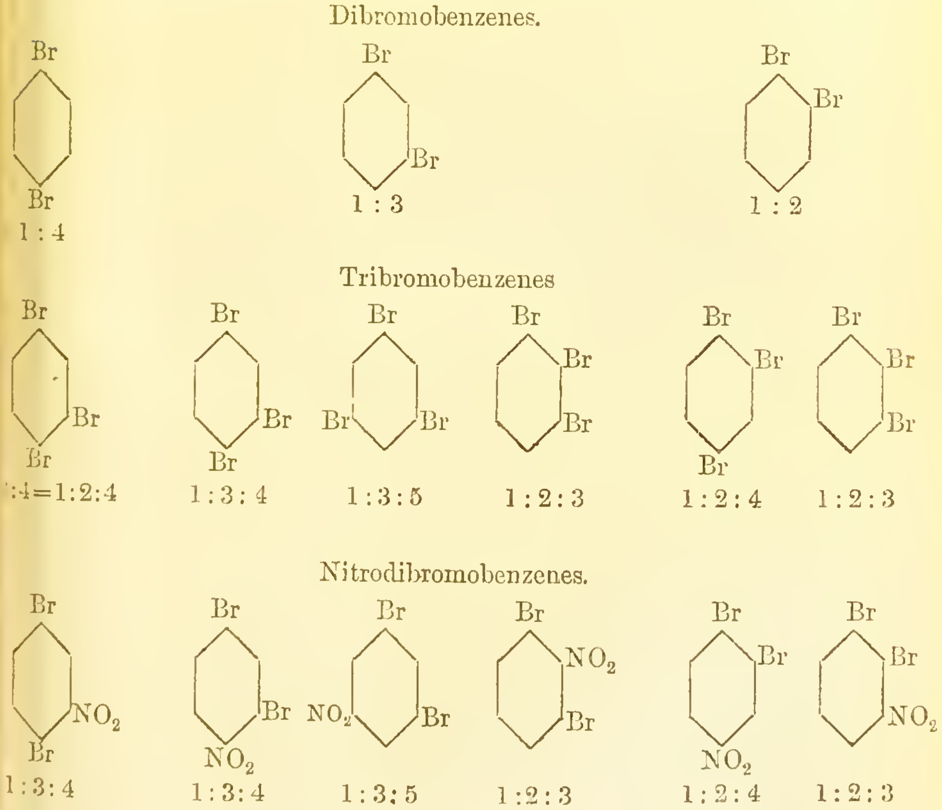
The di-derivatives of benzene, *e.g.*, C_6H_4ClCl, C_6H_4ClBr, $C_6H_4Cl(NO_2)$, &c., exhibit, as above mentioned, three such modifications, which are distinguished by the prefixes *ortho*, *meta*, and *para*: thus the three dichlorobenzenes are designated as follows:

			1	2	3	4	5	6
Orthodichlorobenzene,	1 : 2	. . C_6	Cl	Cl	H	H	H	H
Metadichlorobenzene,	1 : 3	. . C_6	Cl	H	Cl	H	H	H
Paradichlorobenzene,	1 : 4	. . C_6	Cl	H	H	Cl	H	H.

The following are the principal or typical representatives of these three series of compounds:

		1 : 2	1 : 3	1 : 4
Dihydroxybenzenes or Oxyphenols,	$C_6H_4(OH)_2$	Pyrocatechin	Resorcin	Hydroquinone
Oxy-acids,	$C_6H_4<^{OH}_{CO_2H}$	Salicylic	Oxybenzoic	Paraoxybenzoic
Dimethyl-benzenes,	$CH_{64}(CH_3)_2$	Orthoxylene	Metaxylene	Paraxylene
Dicarbon-acids,	$C_6H_4(CO_2H)_2$	Phthalic	Isophthalic	Terephthalic

The relative positions of the substituted radicles in a di-derivative of benzene may be determined by comparison with those in the tri-derivatives which may be formed from it or converted into it. The principle of this method may be illustrated by the case of the di-bromobenzenes, $C_6H_4Br_2$. These, by the action of nitric acid, may be converted into six different nitrodibromobenzenes, $C_6H_3Br_2(NO_2)$; these latter, treated with reducing agents, yield the six corresponding amido-dibromobenzenes, $C_6H_3Br_2(NH_2)$, in which the NH_2 takes the place of the NO_2; and the amido-dibromobenzenes (dibromanilines) treated by processes hereafter to be described, exchange their NH_2 for H, whereby they are reconverted into dibromobenzenes, and for Br, whereby they yield tribromobenzenes. The relations between these di- and tri-derivatives are shown in the following diagram, in which, for simplicity, the C's and H's of the benzene-molecule are omitted, and only the substituted radicles are shown in their relative places; the several tribromo- and nitrodibromobenzenes are placed vertically under the dibromobenzenes from which they are derived.



An inspection of this diagram shows: (1). That a para-derivative (1 : 4) can give rise to, or be derived from, only *one* tri-derivative, viz., the unsymmetrical modification, 1: 2: 4 or 1: 3: 4.

(2). That an ortho-derivative (1: 2) can give rise to, or be produced from, *two* tri-derivatives, viz., the consecutive 1: 2: 3, and the unsymmetrical 1: 2: 4.

(3). That a meta-derivative (1 : 3) can give rise to, or be formed from, all the three tri-derivatives, 1 : 2 : 3, 1 : 3 : 4, and 1 : 3 : 5.

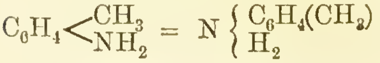
These conclusions, which are fully borne out by experiment, enable us to give definitions of the three classes of di-derivatives depending only on their relations to the tri-derivatives, and independent of all assumptions as to the relative positions of the substituted radicles ; thus:

A di-derivative of benzene is para-, ortho-, or meta-, according as it can give rise to, or be formed from, one, two, or three tri-derivatives.

II. *In the Substitution-derivatives of the Homologues of Benzene.*—The derivatives of toluene and the higher hydrocarbons of the series C_nH_{2n-6}, exhibit two kinds of isomerism: (1). According as the replacement of the hydrogen takes place in the benzene-nucleus or principal chain, or in one of the lateral chains (p. 419); thus from toluene, $C_6H_5.CH_3$, are derived :

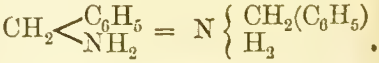
$C_6H_4Cl.CH_3$ Monochlorotoluene.	isomeric with	$C_6H_5.CH_2Cl$ Benzyl chloride.
$C_6H_4(OH).CH_3$ Cresol.	„	$C_6H_5.CH_2(OH)$ Benzyl alcohol.
$C_6H_4(NH_2).CH_3$ Toluidine.	„	$C_6H_5.CH_2(NH_2)$ Benzylamine.

These isomeric derivatives differ considerably from one another in their properties. Those in the left-hand column, formed by replacement of hydrogen in the benzene-nucleus,—like those derived in like manner from benzene itself,—are comparatively stable compounds, which do not give up their chlorine, hydroxyl, &c., in exchange for other radicles so easily as the corresponding derivatives of the paraffins,—whereas those in the right hand column, formed by replacement of hydrogen in the lateral chain, are more active bodies, easily susceptible of this kind of transformation. Thus benzyl alcohol treated with hydrochloric acid yields benzyl chloride (just as ordinary ethyl alcohol similarly treated yields ethyl chloride); and this compound heated with ammonia yields benzylamine ; the chloride is also easily converted into the acetate, cyanide, &c., by treatment with the corresponding potassium salts. In short, these last-mentioned toluene derivatives exhibit reactions exactly like those of the corresponding compounds of the methyl and ethyl groups. The two series of compounds may, however, be represented by formulæ of similar structure, but containing isomeric radicles, C_7H_7, those in the left hand column being compounds of methylphenyl or tolyl, $C_6H_4(CH_3)$, and those in the right-hand column being compounds of phenyl-methyl or benzyl, $CH_2(C_6H_5)$; *e.g.*:



$$C_6H_4 < {}^{CH_3}_{NH_2} = N \left\{ \begin{matrix} C_6H_4(CH_3) \\ H_2 \end{matrix} \right.$$

Toluidine or Tolylamine.



$$CH_2 < {}^{C_6H_5}_{NH_2} = N \left\{ \begin{matrix} CH_2(C_6H_5) \\ H_2 \end{matrix} \right. .$$

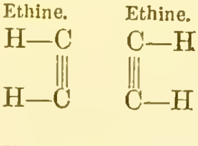
Benzylamine

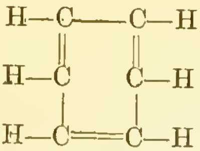
(2). According to the orientation of the substituted radicles in the benzene-nucleus.—This kind of isomerism is of course exhibited only by derivatives like those in the left-hand column, including the hydrocarbons which contain more than one lateral chain; thus: dimethyl-benzene or xylene, $C_6H_3(CH_3)_2$, exhibits the three modifications, 1:2, 1:3, and 1:4.

The difference in chemical character arising from substitution in the principal or in the lateral chains is much greater than that which depends on the orientation of the substituted radicles in the principal chain; in fact, the differences in the latter case are chiefly of physical character, relating to density, melting point, boiling point, &c. In speaking of these two kinds of modification, it will be convenient to designate the former as metameric, the latter as isomeric.

Benzene, C_6H_6.—This hydrocarbon can be produced synthetically from its elements. When ethine or acetylene, C_2H_2, which, as we have seen (p. 61), may be formed by the direct combination of carbon and hydrogen, is heated to a temperature somewhat below redness, it is converted into several polymeric modifications, the principal of which is triethine or benzene, $3C_2H_2 = C_6H_6$.

This mode of formation leads at once to the constitutional formula of benzene above given: for suppose three molecules of ethine placed as in the left hand figure below; and, further, that one of the three units of affinity between the two carbon-atoms in each of these molecules is removed, and employed in linking together the alternate carbon-atoms: then we have the formula of benzene, as given in the right hand figure.





Benzene.

Benzene is also formed in the dry distillation of many organic substances, and is contained in considerable quantity in the more volatile portion of coal-tar oil, from which it is now almost always prepared. To obtain it, the oil is repeatedly washed with dilute sulphuric acid and with potash, to remove the alkaline and acid products likewise existing in it; and the remaining neutral oil is submitted to repeated fractional distillation, the portion which goes over between 80° and 90° being collected apart. On cooling this distillate to −12°, the benzene crystallises out, and may be purified from adhering liquid substances by pressure. It is now prepared in immense quantities for the manufacture of aniline; but the commercial product is always impure, containing also the higher members of the series.

Pure benzene may be obtained by distilling benzoic acid with lime:

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Lime.}}{CaO} = \underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Benzene.}}{C_6H_6}$$

Benzene is identical with the so-called *bicarburet of hydrogen*, discovered many years ago by Faraday in the liquid condensed during the compression of oil-gas (i. 176).

Pure benzene is a thin, limpid, colourless, strongly refracting liquid, having a peculiar ethereal odour. It has a density of 0·889 at 0°, 0·885 at 15·5°, boils at 80·5°, and solidifies at 0° to a mass of rhombic crystals melting at 3°. It is nearly insoluble in water, but mixes with alcohol and ether. It dissolves iodine, sulphur, and phosphorus, and a large number of organic substances, fats and resins for example, which are insoluble, or very sparingly soluble in water and alcohol: hence its use in many chemical preparations, and for removing grease-spots from articles of dress.

Benzene, passed in the state of vapour through a porcelain tube heated to bright redness, is partly resolved into hydrogen gas containing a small quantity of ethine, and the following liquid products: (1.) diphenyl, $C_{12}H_{10} = 2C_6H_6 - H_2$; (2.) diphenylbenzene, $C_6H_4(C_6H_5)_2$, formed according to the equation $3C_6H_6 = C_{18}H_{14} + 2H_2$; (3.) benzerythrene, a solid, resinous, orange-coloured body of unknown composition, which distils over in yellow vapours at a dull red heat; (4.) bitumene, a blackish liquid, which remains in the retort at a dull red heat, and solidifies on cooling.* Heated to 275°–280° with 80–100 parts of strong hydriodic acid, it is converted into hexane, C_6H_{14}.

ADDITIVE-COMPOUNDS OF BENZENE.—Benzene, though, as already observed, it mostly reacts as a saturated molecule—exhibiting indeed in its chemical relations a very close resemblance to the paraffins—can nevertheless, under certain circumstances, take up 6 atoms, or 3 molecules, of chlorine or bromine, forming the compounds $C_6H_6Cl_6$ and $C_6H_6Br_6$. These are crystalline bodies, obtained by exposing benzene to sunshine in contact with chlorine or bromine, the former also by mixing the vapour of boiling benzene with chlorine. Benzene hexchloride melts at 132°, and boils at 288°, being partly resolved at the same time into hydrochloric acid and trichlorobenzene: $C_6H_6Cl_6 = 3HCl + C_6H_3Cl_3$. The same decomposition is quickly produced by heating the compound with alcoholic solution of potash. Benzene hexbromide exhibits a similar reaction.

Benzene is also capable of uniting directly with three molecules of *hypochlorous acid*, forming the compound $C_6H_9Cl_3O_3$, or $C_6H_6.3ClOH$, which crystallises in thin colourless plates melting at about 10°, and is converted by alkalis into a white deliquescent compound called phenose, $C_6H_{12}O_6$, isomeric with glucose or grape-sugar:

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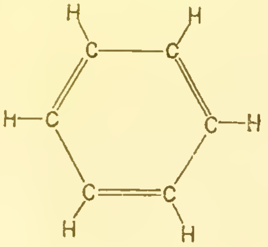
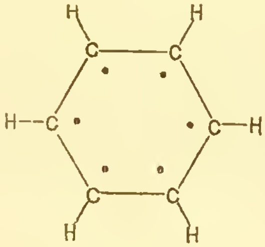
* Berthelot, Bulletin de la Société Chimique de Paris [2], vi. pp. 272, 279; Schultz, Ann. Chem. clxxiv. 201.

$$C_6H_9Cl_3O_3 + 3HKO = 3KCl + C_6H_{12}O_6.$$

The formation of these additive compounds may be explained in the same manner as that of ethene chloride (p. 54), namely, by supposing that when the benzene-molecule is subjected to the influence of chlorine, bromine, &c., the attachment of the alternate pairs of carbon-atoms is loosened, so that each pair of carbon-atoms becomes united by only one unit of affinity, and each carbon-atom has one unit of affinity left free, and ready to take up an atom of chlorine or other univalent radicle. The nature of the alteration is shown by the following figures, in the second of which the unsaturated affinities are indicated by dots:



Saturated.



Unsaturated.

Toluene, C_7H_8, or **Methyl-benzene**, $C_6H_5(CH_3)$.—This hydrocarbon is produced: Synthetically (1.) By the action of sodium on a mixture of bromobenzene (phenyl bromide), and methyl iodide:

$$C_6H_5Br + CH_3I + Na_2 = NaBr + NaI + C_6H_5.CH_3.$$

This reaction is an example of a general synthetical method of producing the hydrocarbons C_nH_{2n-6}, represented by the equation:

$$C_nH_{2n-7}Br + C_nH_{2n+1}I + Na_2 = NaBr + NaI$$
$$+ C_nH_{2n-7}.C_nH_{2n+1} [= C_{2n}H_{4n-6}.]$$

(2.) By the mutual action of benzene and methane in the nascent state, as when a mixture of 2 parts of sodium acetate and 1 part of sodium benzoate is subjected to dry distillation:

$$C_6H_6 + CH_4 = C_7H_8 + H_2.$$

It is also produced by distilling toluic acid, $C_8H_8O_2$, with lime, which abstracts carbon dioxide:

$$C_8H_8O_2 = CO_2 + C_7H_8.$$

It occurs, together with benzene and the other hydrocarbons of the series, in light coal-tar oil, and in the products of the distillation of wood, Tolu balsam, dragon's blood, and other vegetable substances; and, together with many other hydrocarbons, in Rangoon tar or Burmese naphtha.

Toluene is a limpid liquid, smelling like benzene, and having a density of 0·882 at 0°. It boils at 111°, and does not solidify at −20°. In respect of solubility and solvent power, it is very much like benzene, but dissolves somewhat more readily in alcohol. When treated with oxidising agents, it yields benzoic acid, $C_7H_6O_2$, or derivatives thereof; with potassium chromate and sulphuric acid, it yields benzoic acid; and by prolonged boiling with strong nitric acid, nitrobenzoic acid.

Toluene vapour passed through a red-hot porcelain tube is partly resolved into hydrogen gas (with small quantities of methane and ethine), and the following liquid products; (1.) Benzene and naphthalene in considerable quantities. (2.) A crystallisable hydrocarbon volatilising at 280°, and probably consisting of dibenzyl, $C_{14}H_{14}$. (3.) A liquid isomeric with the last. (4.) A mixture, distilling above 360°, of anthracene with an oily liquid. (5.) Chrysene and the last decomposition-products of benzene. The formation of benzene, naphthalene, anthracene, and dibenzyl is represented by the equations:

$$\underset{\text{Toluene.}}{2C_7H_8} = \underset{\text{Dibenzyl.}}{C_{14}H_{14}} + H_2; \quad \underset{\text{Toluene.}}{2C_7H_8} = \underset{\text{Anthracene.}}{C_{14}H_{10}} + 3H_2.$$

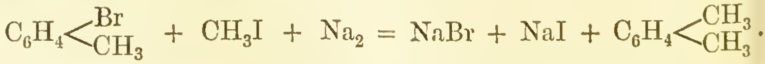
$$\underset{\text{Toluene.}}{4C_7H_8} = \underset{\text{Benzene.}}{3C_6H_6} + \underset{\text{Naphthalene.}}{C_{10}H_8} + 3H_2.$$

Hydrocarbons, C_8H_{10}.—This formula includes the two metameric bodies:

$$\underset{\text{Ethyl-benzene.}}{C_6H_5(CH_2CH_3)} \qquad \underset{\text{Dimethyl-benzene.}}{C_6H_4(CH_3)_2}.$$

1. ETHYL-BENZENE is produced by the action of sodium on a mixture of monobromobenzene and ethyl bromide. It is a colourless, mobile liquid, very much like toluene, having a density of 0·866, and boiling at 134°. By oxidation with chromic acid mixture it yields benzoic acid. It is attacked by chlorine, bromine, and nitric acid, forming substitution-products.

2. DIMETHYL-BENZENE, or XYLENE, admits of the three modifications, para-, ortho-, and meta. The first and second are produced by the action of sodium on a mixture of methyl iodide with para- and ortho-bromotoluene respectively, the bromine-atom in each case being replaced by methyl:



$$C_6H_4{<}\begin{smallmatrix}Br\\CH_3\end{smallmatrix} + CH_3I + Na_2 = NaBr + NaI + C_6H_4{<}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}.$$

Orthoxylene is also formed by heating orthodimethyl-benzoic acid, $C_9H_{10}O_2 = C_6H_3\left\{\begin{matrix}(CH_3)_2\\CO_2H\end{matrix}\right.$ (inappropriately called paraxylic acid), with lime; $C_9H_{10}O_2 = CO_2 + C_8H_{10}$, and metaxylene (or isoxylene) in like manner from two other modifications of the same acid, called xylic and mesitenic acids :

		1-	2	3	4-	5	6	
Paraxylic acid,	C_6.	CH_3.	CH_3.	H.	CO_2H.	H.	H,	give 1:3 Xylene.
Xylic acid,	C_6.	CH_3.	H.	CH_3.	CO_2H.	H.	H,	gives 1 : 2 Xylene.
Mesitenic acid,	C_6.	CH_3.	H.	CH_3.	H.	CO_2H.	H,	

These isomeric xylenes are colourless, volatile liquids, orthoxylene boiling at 140°–141°, metaxylene at 137°, and paraxylene at 136°–137°. Meta- and para-xylene are contained in the less volatile portion of light coal-naphtha. When the portion of this liquid which boils at about 141° is shaken with oil of vitriol containing a little fuming sulphuric acid, the xylene is dissolved in the form of xylene-sulphonic acid, $C_8H_{10}SO_3$; and on decomposing this compound by dry distillation, and purifying the distillate by washing, drying, and rectification, a mixture of metaxylene and paraxylene is obtained, containing 90 per cent. of the former.

Xylene (either modification) passed through a red-hot tube, is resolved into a mixture of several hydrocarbons, among which are benzene, toluene, styrolene, naphthalene, anthracene, and its higher homologues. The formation of some of these products is represented by the following equations:

$$C_8H_{10} - H_2 = C_8H_8 \quad \text{(Styrolene)}$$
$$3C_8H_{10} - 3H_2 = 2C_7H_8 + C_{10}H_8 \quad \text{(Naphthalene)}$$
and
$$2C_7H_8 - 3H_2 = C_{14}H_{10} \quad \text{(Anthracene).}$$

The xylenes, oxidised with a mixture of potassium dichromate and sulphuric acid, are converted into phthalic acids, $C_8H_6O_4$ or $C_6H_4\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$, according to the equation, $C_8H_{10} + O_6 = 2H_2O + C_8H_6O_4$, each modification of the hydrocarbon yielding a corresponding modification of the acid.

Hydrocarbons, C_9H_{12}.—This formula includes the three following metameric bodies :

$$C_6H_5(C_3H_7) \qquad C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right. \qquad C_6H_3\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$$

Propyl-benzene. Ethyl-methyl-benzene. Trimethyl-benzene.

All three have been formed synthetically, the first by the action of sodium and propyl iodide on bromobenzene ; the second by that of sodium and ethyl bromide on bromotoluene ; the third by that of sodium and methyl bromide on bromoxylene ; thus :

(1.) $C_6H_5Br + C_3H_7I + Na_2 = NaBr + NaI + C_6H_5(C_3H_7)$
(2.) $C_6H_4Br(CH_3) + C_2H_5Br + Na_2 = 2NaBr + \; + C_6H_4(CH_3)(C_2H_5)$.
(3.) $C_6H_3Br(CH_3)_2 + CH_3Br + Na_2 = 2NaBr + \; + C_6H_3(CH_3)_3$.

1. Propyl-benzene is a liquid which boils at 157°, forms with excess of bromine a viscid tetrabrominated compound, $C_9H_8Br_4$, and with excess of strong nitric and sulphuric acids, a crystalline tri-nitro-derivative, $C_9H_9(NO_2)_3$.

A hydrocarbon, called cumene, also having the composition C_9H_{12}, and very much like propyl-benzene, exists ready-formed in Roman cumin-oil, and is obtained artificially by distilling cumic acid, $C_{10}H_{12}O_2$, with lime; but it boils at a lower temperature, viz., 151°, forms with bromine a finely crystallised pentabrominated derivative, $C_9H_7Br_5$, and is converted by excess of a mixture of nitric and sulphuric acids only into dinitrocumene, $C_9H_{10}(NO_2)_2$. It agrees with propyl-benzene, however, in being converted by oxidation with chromic acid into benzoic acid. Hence it is probable that both these hydrocarbons have the composition $C_6H_5.C_3H_7$; but that cumene consists of *isopropyl-benzene*, $C_6H_5.CH(CH_3)_2$, whereas the compound formed by the action of sodium and propyl iodide on bromobenzene is *normal propyl-benzene*, $C_6H_5.CH_2CH_2CH_3$. This supposition is in accordance with the lower boiling point of cumene, as it is a general rule that isopropyl-compounds boil at lower temperatures than the corresponding normal propyl-compounds.

Cumene dissolves in hot fuming nitric acid, and water added to the solution throws down a heavy oil, consisting of mononitro-cumene, $C_9H_{11}(NO_2)$, which is reduced by ammonium sulphide to amidocumene or cumidine, $C_9H_{11}(NH_2)$.

2. ETHYL-METHYL-BENZENE or ETHYL-TOLUENE is known in two isomeric modifications. The *para*-modification (1 : 4), obtained from parabromotolnene and ethyl bromide in the same manner as ethyl-benzene from bromobenzene, is a liquid boiling at 161°–162°, and having a density of 0·865 at 21°. By oxidation it yields terephthalic acid. The *meta*-modification (1 : 3), obtained in like manner from metabromotoluene, boils at 158°–159°; has a density of 0·869 at 20°; and is converted by oxidation into isophthalic acid.

3. TRIMETHYL-BENZENE, $C_6H_3(CH_3)_3$, is susceptible of three isomeric modifications, only two of which, however, are known. Both of them exist in coal-tar, but cannot be completely separated therefrom by fractional distillation.

Mesitylene or Symmetrical Trimethyl-benzene, $C_6.CH_3.H.CH_3.H.CH_3.H$, is formed by distilling acetone with sulphuric acid:

$$3CO(CH_3)_2 = C_6H_3(CH_3)_3 + 3H_2O\,.$$

A mixture of 1 vol. acetone and 1 vol. sulphuric acid, diluted with $\frac{1}{2}$ vol. water, is distilled from a retort containing sand, and the oily layer of the distillate is separated from the watery layer, washed with solution of sodium carbonate, and distilled.

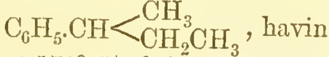
Mesitylene is a colourless, fragrant liquid, boiling at 163°. By oxidation with dilute nitric acid, it is successively converted into mesitylenic acid, $C_6H_3(CH_3)_2CO_2H$, mesidic or uvitic acid,

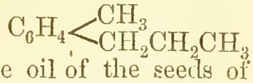
$C_6H_3(CH_3)(CO_2H)_2$, and trimesic acid, $C_6H_3(CO_2H)_3$, all of which have the symmetrical structure 1 : 3 : 5. By oxidation with chromic acid mixture it is completely decomposed, with formation of acetic acid. Heated with phosphonium iodide, PH_4I, to 250°–300°, it is converted into the hydrocarbon, C_9H_{18}, which boils at 136°, and yields, with oxidising agents, the same products as mesitylene itself.

Pseudocumene or Unsymmetrical Trimethyl-benzene, $C_6.CH_3.H.CH_3.CH_3.H_2$, occurs, together with mesitylene, in coal-tar oil (boiling at 162°–168°), and is formed by the action of methyl iodide and sodium on bromoparaxylene, $C_6.CH_3.H.Br.CH_3.H_2$, or bromometaxylene, $C_6.CH_3.H.CH_3.Br.H_2$. It boils at 166°, and is oxidised by dilute nitric to paraxylic acid, $C_6H_3(CH_3)_2CO_2H$, and xylidic acid, $C_6H_3(CH_3)(CO_2H)_2$.

Hydrocarbons, $C_{10}H_{14}$.—Of these there are five metameric modifications, viz. :—

Butyl-benzene, ...	$C_6H_5.C_4H_9$
Methyl-propyl-benzene, ...	$C_6H_4.CH_3.C_3H_7$
Diethyl-benzene, ...	$C_6H_4.C_2H_5.C_2H_5$
Ethyl-dimethyl-benzene, ...	$C_6H_3.C_2H_5.(CH_3)_2$
Tetramethyl-benzene, ...	$C_6H_2(CH_3)_4$

1. BUTYL-BENZENE.—Of this hydrocarbon there are three sub-modifications depending upon the structure of the butyl-radicle. *Normal butyl-benzene*, $C_6H_5.CH_2.CH_2.CH_2.CH_3$, and *Isobutyl-benzene*, $C_6H_5.CH_2.CH(CH_3)_2$, are obtained by the action of sodium on a mixture of bromobenzene and normal or isobutyl bromide, or on a mixture of benzyl bromide ($C_6H_5.CH_2Br$), or chloride, with the iodide of normal propyl or isopropyl. The first has a density of 0·8622 at 16°, and boils at 180° ; the second has a density of 0·89 at 15°, and boils at 167·5°. A third *butyl-benzene*,  $C_6H_5.CH{<}\begin{smallmatrix}CH_3\\CH_2CH_3\end{smallmatrix}$, having a density of 0·8726 at 16°, and boiling at 170°–172°, is produced by the action of zinc-ethyl on phenyl-ethyl bromide, $C_6H_5.CHBr.CH_3$.

2. METHYL-PROPYL-BENZENE or CYMENE,  $C_6H_4{<}\begin{smallmatrix}CH_3\\CH_2CH_2CH_3\end{smallmatrix}$ (1 : 4), occurs in Roman cumin oil (the volatile oil of the seeds of *Cuminum Cyminum*), and in the volatile oils of *Ptychotis Ajowan*, *Cicuta virosa*, *Eucalyptus globulus*, and other plants. It is produced synthetically by the action of sodium on a mixture of parabromotoluene and normal propyl iodide; formed also from turpentine oil and its isomerides, $C_{10}H_{16}$, by heating with iodine, by the action of strong sulphuric acid, and by heating the dibromides of these hydrocarbons with sodium, alcoholic potash, or aniline. It appears also to be formed in small quantity by the spontaneous oxidation of turpentine oil in contact with the air. Further, it is produced from the isomeric compounds, thymol and carvacrol, $C_6H_3(OH)(CH_3)(C_3H_7)$, by heating with phosphorus pentasul-

phide, or by the action of phosphorus pentachloride and sodium-amalgam, chlorocymene being first produced and then dechlorinated by the sodium-amalgam; lastly, together with toluene, xylene, mesitylene, and other hydrocarbons, by distilling camphor, $C_{10}H_{16}O$, over zinc chloride or phosphoric anhydride. It is most easily prepared by gently heating two parts of camphor with one part of phosphorus pentasulphide, repeatedly agitating the crude distillate with strong sulphuric acid, and rectifying.

Cymene is a liquid having a specific gravity of 0·8732 at 0°, and boiling at 175°. By oxidation with nitric and with chromic acid, it yields paratoluic and terephthalic acids. It dissolves in strong sulphuric acid, forming a sulphonic acid, the barium salt of which crystallises in shining laminæ, having the composition $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$.

3. Diethyl-benzene, $C_6H_4(C_2H_5)_2$ (1 : 4), obtained by the action of sodium on a mixture of bromethyl-benzene and ethyl bromide, is a colourless liquid which boils at 178°–179°, and is converted by oxidation into ethyl-benzoic acid (1 : 4) and terephthalic acid.

4. Ethyl-dimethyl-benzene or Ethyl-xylene, $C_6H_3\left\{\begin{matrix} C_2H_5 \\ (CH_3)_2 \end{matrix}\right.$, is formed, together with methyl-diethyl-benzene, by distilling a mixture of dimethyl ketone (acetone) and methyl-ethyl ketone with sulphuric acid: hence, like mesitylene, it possesses the symmetrical structure, 1 : 3 : 5 (p. 430). It has a density of 0·864 at 20°, boils at 180°–182°, and is oxidised by nitric acid to mesitylene and uritic acids.

5. Tetramethyl-benzene or Durene, $C_6H_2(CH_3)_4$ (consecutive or symmetrical ?), is formed by the action of sodium on a mixture of methyl-iodide and bromopseudocumene on dibromoxylene. It is crystalline at ordinary temperatures, melts at 79°–80°, boils at 190°, and is oxidised by dilute nitric acid to durylic acid, $C_6H_2(CH_3)_2CO_2H$, and cumidic acid, $CH(CH_3)_2(CO_2H)_2$.

The unsymmetrical modification (1 : 3 : 4 : 5), obtained from bromomesitylene, boils at 192°–194°, and remains liquid at low temperatures.

Hydrocarbons, $C_{11}H_{16}$.—Of the seven metameric compounds represented by this formula, three only have been obtained, viz.:

Amyl-benzene, ...	$C_6H_5.C_5H_{11}$	boiling at	193°
Diethyl-methyl-benzene, or Diethyl-toluene, ...	$C_6H_3\left\{\begin{matrix} CH_3 \\ (C_2H_5)_2 \end{matrix}\right.$	”	178°
Propyl-dimethyl-benzene, Propyl-xylene or Laurene, . . .	$C_6H_3\left\{\begin{matrix} (CH_3)_2 \\ C_3H_7 \end{matrix}\right.$	”	188°

The first is obtained by the action of sodium on a mixture of monobromobenzene and amyl bromide; the second by that of zinc-ethyl on benzylene chloride:

$$C_6H_5.CHCl_2 + Zn(C_2H_5)_2 = ZnCl_2 + C_6H_3.CH_3(C_2H_5)_2;$$

the third, together with several of its lower homologues, by distilling camphor with zinc chloride. The constitution of this last modification is inferred from its reaction with dilute nitric acid, which oxidises it to lauroxylic acid, $C_9H_{10}O_2$:

$$C_6H_3\left\{\begin{matrix}(CH_3)_2\\ C_3H_7\end{matrix}\right. + O_9 = 2CO_2 + 3H_2O + C_6H_3\left\{\begin{matrix}(CH\ )_2\\ CO_2H\end{matrix}\right. .$$

Hydrocarbons, $C_{12}H_{18}$ and $C_{13}H_{20}$.—These bodies admit of numerous modifications, but the first is known in only two, the second in one modification, viz.:

		Boiling point.	Specific gravity at 9°.
Triethyl-benzene, . .	$C_6H_3(C_2H_5)_3$	218°	...
Amyl-methyl-benzene or Amyl-toluene, . . .	$C_6H_4\left\{\begin{matrix}C_5H_{11}\\ CH_3\end{matrix}\right.$	213°	0·8643
Amyl-dimethyl-benzene or Amyl-xylene, . . .	$C_6H_3\left\{\begin{matrix}C_5H_{11}\\ (CH_3)_2\end{matrix}\right.$	233°	0·8951

Triethyl-benzene (1:3:5) is formed by distilling ethyl-methyl ketone, $CH_3—CO—C_2H_5$, with sulphuric acid; it is oxidised by chromic acid to trimesic acid.

Amyl-methyl-benzene and **amyl-dimethyl-benzene** are formed by the action of sodium and amyl bromide on bromotoluene and bromoxylene respectively.

UNSATURATED HYDROCARBONS,

C_nH_{2n-8} and C_nH_{2n-10}.

Ethenyl-benzene or **Vinyl-benzene,** $C_8H_8 = C_6H_5—CH{=}CH_2$; also called *Phenyl-ethene, Cinnamene,* and *Styrolene.* This hydrocarbon occurs in liquid storax (from *Liquidambar orientale*), and may be prepared therefrom by distilling the balsam with water containing a little sodium carbonate, to retain cinnamic acid.

It is produced: 1. Synthetically: *α.* By passing a mixture of benzene-vapour and acetylene or ethene through a red-hot tube:

$$C_6H_6 + C_2H_2 = C_8H_8;\ \text{and}\ C_6H_6 + C_2H_4 = C_8H_8 + H_2.$$

β. In like manner, together with benzene, from diphenyl and ethene:

$$C_{12}H_{10} + C_2H_4 = C_8H_8 + C_6H_6.$$

2. In the decomposition of xylene which takes place when the vapour of that compound is passed through a red-hot tube: $C_8H_{10} = C_8H_8 + H_2$ (p. 429).

3. By distilling cinnamic acid with baryta, which removes carbon dioxide: $C_9H_8O_2 = CO_2 + C_8H_8$.

Cinnamene is a very mobile, colourless oil of specific gravity 0·924. It boils at 146°, and has a density of 0·924. When heated to 200° in a sealed tube, it is converted into a white, transparent, highly refractive, solid substance, called metacinnamene or metastyrolene. This substance, when heated in a small retort, yields a distillate of pure liquid cinnamene.*

A mixture of cinnamene vapour and ethene passed through a red-hot tube yields large quantities of benzene and naphthalene. The first is produced from the cinnamene by abstraction of C_2H_2; the second according to the equation:

$$C_8H_8 + C_2H_4 = C_{10}H_8 + 2H_2 .$$

A mixture of cinnamene and benzene vapours, passed through a red-hot porcelain tube, yields anthracene, $C_{14}H_{10}$, together with small quantities of other products:

$$C_8H_8 + C_6H_6 = C_{14}H_{10} + 2H_2 .$$

Cinnamene acts with chlorine and bromine like a bivalent radicle, forming the compounds $C_8H_8Cl_2$ and $C_8H_8Br_2$, which, when treated with alcoholic potash, give up HCl and HBr (like the corresponding ethene-compounds), leaving chloro-cinnamene, C_8H_7Cl, and bromo-cinnamene, C_8H_7Br. According to Laurent, cinnamene yields with chlorine a hexchloride of dichloro-cinnamene, $C_8H_6Cl_2.Cl_6$.—Metacinnamene is also acted upon by bromine, but with considerable difficulty.—Both cinnamene and metacinnamene treated with fuming nitric acid yield mononitrated derivatives, $C_8H_7(NO_2)$: that obtained from cinnamene is crystalline; that from metacinnamene amorphous.

Allyl-benzene, $C_9H_{10} = C_6H_5—CH_2—CH{=}CH_2$, or *Phenyl-allyl*, formed by heating bromobenzene (phenyl bromide), C_6H_5Br, and allyl bromide, C_3H_5Br, with zinc, boils at 155°, and forms a dibromide melting at 60°.

Phenyl-propylene, $C_6H_5—CH{=}CH—CH_3$, isomeric with it, is obtained from cinnamic alcohol; it boils 170°, and forms a dibromide melting at 66°.

Acetenyl-benzene or **Phenyl-acetylene,** $C_8H_6 = C_6H_5—C{\equiv}CH$, is formed by heating bromocinnamene, $C_6H_5 . CH{=}CHBr_2$ or acetophenone chloride, $C_6H_5.CCl_2.CH_3$, with alcoholic potash; also by heating phenylpropiolic acid to 120°, with water or with baryta:

$$C_6H_5—C{\equiv}C—CO_2H = CO_2 + C_6H_5—C{\equiv}CH ;$$

further, together with cinnamene, by the action of heat on several hydrocarbons. It is an aromatic liquid, boiling at 140°, and precipitating ammoniacal silver and copper solutions, like acetylene. The *copper-compound*, $(C_8H_5)_2Cu_2$, is yellow: the *silver-compound*, $(C_8H_5)_2Ag_2.Ag_2O$, is white. Sodium dissolves in it, forming the compound, C_8H_5Na, which takes fire on coming in contact with the air, and is converted by carbonic acid passed into its ethereal solution, into the sodium salt of phenylpropiolic acid.

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* It was formerly supposed that cinnamene prepared from cinnamic acid was not converted by heat into a solid modification, like styrolene from storax: hence the two were regarded as isomeric, not identical; but later researches have shown that pure cinnamene from cinnamic acid is likewise convertible into solid metacinnamene.

On shaking up the copper-compound with alcoholic ammonia, *diacetenyl-phenyl*, $(C_6H_4.C_2H)_2$ or $CH{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CH$, separates out. This compound, isomeric with pyrene, melts at 97°, and forms a crystalline compound with picric acid.

Ethyl-acetenyl-benzene, $C_{10}H_{10} = C_6H_5{-}C{\equiv}C{-}C_2H_5$, obtained by the action of ethyl iodide on the sodium-compound of acetenyl-benzene, is a colourless liquid having a density of 0·923 at 21°, and boiling at 201°–203°.

HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.

These compounds are formed: (1.) By direct substitution of the halogen elements. Chlorine and bromine act on the aromatic hydrocarbons more readily than on the paraffins, especially in presence of iodine, which acts as a carrier of the chlorine or bromine. The action of chlorine is further promoted by the presence of a small quantity of antimony pentachloride, or molybdenum pentachloride, these bodies first giving up a portion of their chlorine to the hydrocarbon, whereby they are reduced to lower chlorides, which then take up an additional quantity of chlorine, and transfer it in like manner.

Iodine-derivatives cannot be obtained by the action of iodine alone, because, as in the case of the iodo-paraffins (p. 65), the substitution-product, if formed, would be immediately decomposed by the hydriodic acid formed at the same time. The reverse action may, however, be prevented by addition of iodic acid, the action taking place as represented by the equation:

$$5C_6H_6 + 2I_2 + IO_3H = 5C_6H_5I + 3H_2O.$$

(2.) By the action of pentachloride, pentabromide, or pentiodide of phosphorus on the hydroxyl-derivatives of the hydrocarbons (phenols and alcohols); *e.g.*,

$$\underset{\text{Cresol.}}{C_7H_7(OH)} + PCl_5 = \underset{\text{Chloro-toluene.}}{C_7H_7Cl} + POCl_3 + HCl.$$

(3.) By the decomposition of substituted aromatic acids by heat; *e.g.*,

$$\underset{\text{Chlorobenzoic acid.}}{C_6H_4Cl.CO_2H} = CO_2 + \underset{\text{Chlorobenzene.}}{C_6H_5Cl}$$

(4.) The halogen-derivatives of benzene may be formed from amidobenzene, $C_6H_5.NH_2$ (aniline), and the chloranilines, &c., $C_6H_4Cl.NH_2$, for example, by exchange of the group NH_2 for Cl, Br, &c., through the medium of the corresponding diazo-compounds (*q. v.*). This is a very important reaction, serving in many cases to determine the orientation of the halogen-atoms in the di-, tri-, and tetra-derivatives.

Benzene-derivatives.

Chlorobenzenes.—Of these compounds all the possible modifications have been obtained.

Monochlorobenzene, C_6H_5Cl, or *Phenyl chloride*, prepared by chlorination of benzene, or by the action of PCl_5 on phenol, is a liquid of specific gravity 1·128 at 0°, boiling at 132°, solidifying at $-40°$.

Dichlorobenzenes, $C_6H_4Cl_2$.—In the formation of these bodies by direct chlorination of benzene, the ortho- and para-modifications are always formed in preference to the meta ; in fact the latter can, for the most part, be obtained only by indirect methods, as by exchange of the NH_2 in chloraniline for Cl in the manner above mentioned. The same observation applies to the dibromobenzenes.

Ortho- (1:2).—From benzene and chlorine (together with 1:4), and from orthochlorophenol. Colourless liquid, not solidifying at $-19°$. Boiling point 179°; specific gravity $=1·3728$ at 0°.

Meta- (1:3).—From metachloraniline, $C_6.NH_2,H.Cl.H_3$, by exchange of NH_2 for Cl, and from dichloraniline (1 : 2 : 4), $C_6.NH_2.Cl.H.Cl.H_2$, by exchange of NH_2 for H. Liquid, solidifying at $-18°$, boiling at 172°. Specific gravity 1·307 at 0°.

Para- (1:4), the chief product of the action of chlorine on benzene, in presence of iodine, forms colourless, monoclinic crystals, melts at 54°, boils at 173°. Produced also by the action of PCl_5 on parachlorophenol.

Trichlorobenzenes, $C_6H_3Cl_3$.—The *unsymmetrical* modification 1:2:4, obtained by chlorination of benzene, by the action of PCl_5 on dichlorophenol, and from benzene hexchloride, $C_6H_6Cl_6$, by alcoholic potash, which removes 3HCl, forms colourless crystals, melts at 17°, boils at 213°.

The *symmetrical* modification 1:3:5 (or 2:4:6), obtained from trichloraniline, $C_6.\overset{1}{NH_2}.\overset{2}{Cl}.H.\overset{4}{Cl}.H.\overset{6}{Cl}$, by exchange of NH_2 for H, or from dichloraniline, $C_6.\overset{1}{NH_2}.H.\overset{3}{Cl}.H.\overset{5}{Cl}.H$, by exchange of NH_2 for Cl, melts at 63·4°, boils at 208°, sublimes at ordinary temperatures.

The *consecutive* modification 1 : 2 : 3, from trichloraniline, $C_6.NH_2.Cl.Cl.Cl.H_2$, crystallises from alcohol in large plates, melts at 53°–54°, and boils at 218°–219°.

Tetrachlorobenzenes, $C_6H_2Cl_4$.—*Unsymmetrical* (1:3:4:5 or 1:2:4:6), from trichloraniline, $C_6.NH_2.Cl.H.Cl.H.Cl$, forms colourless needles, melts at 50°–51°, boils at 246°.—*Symmetrical* (1:2:4:5), from benzene with chlorine, and from trichloraniline, $C_6.NH_2.Cl.H.Cl.Cl.H$, forms slender needles, melts at 137°–138°, boils at 243°–246°. *Consecutive* (1:2:3:4), from trichloraniline, $C_6.NH_2.Cl.Cl.Cl.H.$, crystallises in needles, melts at 45°–46°, boils at 254°.

Pentachlorobenzene, C_6HCl_5, from benzene with chlorine, melts at 85°, boils at 270°.

Hexchlorobenzene, C_6Cl_6 (Julin's *chloride of carbon*), is formed by chlorination of benzene in presence of iodine, $SbCl_5$, or $MoCl_5$; also by passing the vapour of chloroform or carbon dichloride, C_2Cl_4, through a red-hot tube. Long, thin, colourless prisms; m. p. 222°–226°; b. p. 332°.

Bromobenzenes.—*Monobromobenzene*, C_6H_5Br, from benzene with bromine, and from phenol with PBr_5, is a liquid boiling at 154°, and having a density of 1·519 at 0°.

Dibromobenzenes, $C_6H_4Br_2$.—Direct bromination of benzene (with aid of heat) yields chiefly the para-, with only a small quantity of the ortho-modification.

Para (1:4).—Obtained from benzene, parabromophenol, and parabromaniline, melts at 89°, boils at 218°, and yields a mononitro-derivative melting at 85°.

Meta- (1:3).—From metabromaniline, $C_6.NH_2.H.Br.H_3$, by exchange of NH_2 for Br, and from dibromaniline, $C_6.NH_2.Br.H.Br.H_2$, by exchange of NH_2 for H, is a liquid, boiling at 219°, of specific gravity 1·955 at 18·6°, not solidifying at −20°; yields two mononitro-derivatives, $C_6H_4(NO_2)Br$, one melting at 61°, the other at 82·5°.

Ortho- (1:2), from orthobromaniline, and in small quantity from benzene and bromine. Liquid, solidifying below zero; m. p. −1°; b. p. 223·8°; sp. gr. 2·003 at 0°.

Tribromobenzenes, $C_6H_2Br_3$.—The *unsymmetrical* modifications, 1:2:4 or 1:3:4, is formed by the action of bromine on benzene, and from either of the three dibromobenzenes: hence its constitution is determined (p. 423); also from benzene hexbromide, $C_6H_6Br_6$, by the action of alcoholic potash, which abstracts 3HBr, and from dibromophenol, $C_6.OH.Br.H.Br.H_2$ (exchange of OH for Br by the action of PBr_5). It melts at 44° and boils at 275°. The *symmetrical* modification, 1:3:5, from tribromaniline $C_6.NH_2.Br.H.BrH.Br$, melts at 119·5°, and boils at about 278°. The *consecutive* modification, 1:2:3, from tribromaniline $C_6.NH_2.H.Br.Br.Br.H$, melts at 87°.

Tetrabromobenzenes, $C_6H_2Br_4$.—*Unsymmetrical*, 1:3:4:5, from tribromophenol, $C_6.OH.H.Br.Br.Br.H$, also from the corresponding tribromaniline, and from tetrabromaniline, forms colourless crystals, melting at 98°. The *symmetrical* modification 1:2:4:5, from benzene with bromine, forms colourless needles melting at 137°–140°.

Pentabromobenzene, C_6HBr_5, obtained by the bromination of benzene, forms colourless needles, subliming without decomposition, melting at about 240°.

Hexbromobenzene, C_6Br_6, is formed by the action of bromine on benzene in sunshine, or by heating benzene with bromine containing iodine; also from tetrabromomethane, CBr_4, in small quantity by distillation, in larger quantity by heating to 300°–400° in a sealed tube. Resembles hexchlorobenzene; melts at a temperature above 300°.

It will be seen from the above that all the bromobenzenes are known except consecutive tetrabromobenzene.

Iodobenzenes are obtained by heating benzene with iodine and iodic acid to 200°–240°; by the action of iodine and phosphorus on phenol: by treating silver benzoate with iodine chloride; and from aniline and the iodanilines, similarly to the chlorine compounds.

C_6H_5I is a colourless liquid, boiling at 185°: specific gravity 1·69.

$C_6H_4I_2$.—*Para.* Laminæ; m.p. 127°, b.p. 277°.—*Meta.* Large shining laminæ resembling naphthalene; m.p. 40·4°; b.p. 284·7°.

$C_6H_3I_3$. Needles melting at 76°, and volatilising without decomposition.

Fluobenzene.—C_6H_5F, obtained by heating calcium fluobenzoate with slaked lime, is a scaly crystalline mass, melting at 40°; boils at 180°–183°.

Toluene-derivatives.

These compounds, as already observed, exhibit metameric modifications, according as the replacement of hydrogen atoms takes place in the principal or the lateral chain; and isomeric modifications determined by the orientation of the substituted radicles in the benzene-ringor principal chain (p. 424).

Chlorotoluenes.—Of monochlorinated toluenes there are two metameric modifications, viz.:—

$C_6H_4Cl.CH_3$	$C_6H_5.CH_2Cl$,
Chlorotoluene.	Benzyl chloride.

the first produced by the action of chlorine on toluene at ordinary temperatures or in presence of iodine; the second by the action of chlorine on boiling toluene.

Chlorotoluene or *Tolyl Chloride*, $C_6H_4<^{CH_3}_{Cl}$, admits of three isomeric modifications, according to the relative positions of the chlorine and the methyl-group.—*Parachlorotoluene*, $C_6.CH_3.H.H.Cl.H_2$, the chief product formed by the action of chlorine on toluene at ordinary temperatures, is a liquid solidifying at 0°, melting at 6·5°, and boiling at 160°. By oxidation with nitric acid, or with chromic acid mixture, it is converted into parachlorobenzoic acid:

$$C_6H_4Cl.CH_3 + O_3 = C_6H_4Cl.CO_2H + H_2O.$$

Orthochlorotoluene, $C_6.CH_3.Cl.H_4$, produced in small quantity, together with the para-compound, is a liquid, boiling at 156°, and completely decomposed by chromic acid, without formation of a chlorobenzoic acid.—*Metachlorotoluene*, $C_6.CH_3.H.Cl.H_3$, is prepared from chloroparatoluidine, $C_6.CH_3.H.Cl.NH_2.H_2$, by exchange of NH_2 for H, and converted by oxidation into metachlorobenzoic acid.

Benzyl chloride, $C_6H_5.CH_2Cl$, obtained by the action of chlorine on boiling toluene, and of PCl_5 on benzyl alcohol, $C_6H_5.CH_2OH$, is a liquid which gives off tear-exciting vapours, and boils at 176°. It easily exchanges its chlorine-atom by double decomposition, being converted into acetate, cyanide, &c., by treatment with the corresponding potassium salts. It yields benzoic acid by oxidation, and is converted by heating with water and lead nitrate into benzaldehyde (bitter almond oil).

Of *dichlorotoluene*, $C_7H_6Cl_2$, there are three metamerides, viz.:

$C_6H_3Cl_2.CH_3$	$C_6H_4Cl.CH_2Cl$	$C_6H_5.CHCl_2$.
Dichlorotoluene.	Chlorobenzyl chloride.	Benzal chloride.

The first admits of six isomeric modifications, but only one is known, viz., $C_6.\overset{1}{CH_3}.H.\overset{3}{Cl}.\overset{4}{Cl}.H_2$, which is a liquid, boiling at 196°, formed by chlorination of toluene.—*Chlorobenzyl chloride* admits of three isomerides, one of which is a liquid boiling at 213°–214°.—*Benzal chloride* (also called *chlorobenzol*) is formed by the action of chlorine on boiling toluene, and from benzaldehyde (bitter almond oil) by PCl_5. Liquid having a pungent odour; sp. gr. 1·295 at 16°; boils at 206°; converted into benzaldehyde by heating with water to 20°.

Trichlorotoluenes, $C_7H_5Cl_3$:

$C_6H_2Cl_3CH_3$	$C_6H_3Cl_2.CH_2Cl$	$C_6H_4Cl.CHCl_2$	$C_6H_5.Cl_3$
6 Isomerides.	6 Isomerides.	3 Isomerides.	one.

Trichlorotoluene, $C_6H_2Cl_3.CH_3$, obtained by chlorination of toluene, forms colourless crystals, melts at 76°, boils at 235°.—*Dichlorobenzyl chloride*, $C_6.\overset{1}{(CH_2Cl)}.H.\overset{3}{Cl}.\overset{4}{Cl}.H_2$, is a liquid boiling at 241°.—*Chlorobenzal chloride* (*para.*), $C_6.\overset{1}{(CHCl)_2}.H.H.\overset{4}{Cl}.H_2$, boils at 234°.—*Benzotrichloride*, $C_6H_5.Cl_3$, formed by heating benzoyl chloride, $C_6H_5.COCl$, with PCl_5, boils at 213°–214°.

Of the higher chlorotoluenes, some are liquid, some solid, at ordinary temperatures. The melting and boiling points of the known modifications are given in the following table:

Tetrachlorotoluene, $C_7H_4Cl_4$:

$C_6HCl_4.CH_3$	$C_6H_2Cl_3.CH_2Cl$	$C_6H_3Cl_2.CHCl_2$	$C_6H_4Cl.CCl_3$
m.p. 91–92°; b.p. 271°.	liq. b.p. 273°.	liq. b.p. 257°.	liq. b.p. 245°.

Pentachlorotoluenes, $C_7H_3Cl_5$:

$C_6Cl_5.CH_3$	$C_6HCl_4.CH_2Cl$	$C_6H_2Cl_3.CHCl_2$	$C_6H_3Cl_2.CCl_3$
m.p. 218°; b.p. 301°.	liq. b.p. 296°.	liq. b.p. 280°–281°.	liq. b.p. 273°.

Hexchlorotoluenes, $C_7H_2Cl_6$:

$C_6Cl_5.CH_2Cl$	$C_6HCl_4.CHCl_2$	$C_6H_2Cl_3.CCl_3$
m.p. 103°; b.p. 325°–327°.	liq. b.p. 305°–306°.	m.p. 82°; b.p. 307°–308°.

Heptachlorotoluenes, C_7HCl_7:

$C_6Cl_5.CHCl_2$	$C_6HCl_4.CCl_3$
m.p. 109°; b.p. 334°.	m.p. 104°; b.p. 316°.

When an attempt is made to replace the last hydrogen-atom in toluene by chlorine, the molecule splits up, and perchlorobenzene is produced.

Bromotoluenes.—*Mono-*, $C_7H_7Br = C_6H_4Br.CH_3$.—The ortho- and para- modifications are formed by the action of bromine on toluidine; and all the three modifications from the corresponding amidotoluenes (toluidines) by heating the diazoperbromides with alcohol (see DIAZO-COMPOUNDS).

Ortho-	Colourless liquid: sp. gr. 1·401 at 18°; b. p. 182°–183°.
Meta-	Colourless liquid: sp. gr. 1·4009 at 21°; b. p. 184°.
Para-	Colourless crystals: m. p. 28·5°; b. p. 185°.

Benzyl bromide, $C_6H_5.CH_2Br$, obtained by bromination of toluene at the boiling heat, and by the action of hydrobromic acid on benzyl alcohol, is a liquid which gives off a tear-exciting vapour, has a sp. gr. of 1·438 at 22°, and boils at 201°.

Dibromotoluene, $C_7H_3Br_2.CH_3$, admits of six isomeric modifications, all of which are known. $C_6.CH_3.Br.H.Br.H_2$ (1 : 2 : 4), obtained by direct bromination of toluene, crystallises in needles; melts at 107°–108°; boils at 245°. $C_6.CH_3.H.Br.Br.H_2$ (1 : 3 : 4), formed by the action of bromine in presence of iodine, and in sunshine, is a liquid boiling at 240°. The other four modifications, whose boiling points lie between 237° and 246°, two liquid and two solid (m. p. 42·5° and 60°), are obtained from bromotoluidines, through the medium of the diazo-compounds.

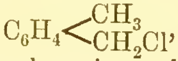
Benzal bromide, $C_6H_5.CHBr_2$, formed by treating bitter almond oil with PBr_5, is a liquid which decomposes when distilled.

Monoiodotoluenes, $C_6H_4I.CH_3$.—The *ortho-* and *meta-*modifications are colourless liquids, the former boiling at 205°, the latter at 207°. *Para-iodotoluene* crystallises in shining laminæ; melts at 35°; boils at 211°. All three give by oxidation the corresponding iodobenzoic acids.

Benzyl iodide, $C_6H_5.CH_2I$, formed from the chloride by the action of hydriodic acid, melts at 24°, and decomposes when sublimed.

Derivatives of the Hydrocarbons, C_8H_{10}.

Ethylbromobenzene, $C_6H_4Br.C_2H_5$, formed by the action of bromine on ethyl-benzene at ordinary temperatures, is a colourless liquid, boiling at 190°.—*Bromethyl-benzene,* $C_6H_5.CHBr.CH_3$ (or $C_6H_5.CH_2.CHBr$), and the corresponding *chloride,* formed by the action of bromine or chlorine with aid of heat, are liquids which decompose when distilled. The chloride, boiled with potassium cyanide and alcohol, is converted into the corresponding *cyanide,* $C_6H_5.CH_2.CH_2(CN)$, a colourless liquid, boiling at 261°, having a sp. gr. of 1·0014 at 18°, and forming the chief constituent of oil of water-cress.

Metaxylyl Chloride,  $C_6H_4{<}\begin{smallmatrix}CH_3\\CH_2Cl\end{smallmatrix}$, obtained by the action of chlorine on boiling metaxylene, is a colourless liquid, boiling at 195°.

Monobromometaxylene, $C_6.Br.CH_3.H.CH_3.H_2$, from metaxylene and bromine, boils at 204°–205°.—An isomeric compound (1 : 3 : 5), formed by the action of nitrous acid and alcohol on bromometaxylidine, is a liquid boiling at 204°, not solidifying at 20°, and having sp. gr. of 1·362 at 20°.

Dibromometaxylene, $C_6H_2Br_2(CH_3)_2$, from metaxylene and bromine, forms colourless shining crystalline scales, m. p. 72°, b. p. 256°. *Tetrabromometaxylene,* $C_6Br_4(CH_3)_2$, forms long slender needles, slightly soluble in alcohol, melting at 241°.

Bromoparaxylene, $C_6H_3Br(CH_3)_2$, forms colourless shining tables; melts at 10°; boils at 200°. *Dibromoparaxylene* melts at 72°, and resembles the meta-compound in all other respects.

Tollylene chloride, $C_6H_4(CH_2Cl)_2$, and **Tollylene bromide,** $C_6H_4(CH_2Br)_2$, formed by the action of chlorine or bromine on boiling paraxylene, crystallise in colourles laminæ. The chloride melts at 100°, and boils, with partial decomposition, at 240°–250°; the bromide melts at 145°–147°. Both compounds, when treated with potassium cyanide in alcoholic solution, yield tollylene cyanide, $C_6H_4\,(CH_2.CN)_2$.

CYANOGEN-DERIVATIVES.

Cyanobenzene, $C_6H_5.CN$ (*Benzonitril, Phenyl Cyanide*), is formed, like the nitrils of the fatty group (p. 92), by dehydration of ammonium benzoate, $C_7H_5O_2.NH_4$, and by distilling the potassium salt of benzenesulphonic acid with potassium cyanide (or the dry ferrocyanide):

$$C_6H_5.SO_3K + KCN = SO_3K_2 + C_6H_5CN;$$

also by heating phenyl isocyanide with metallic copper, and by other reactions. It is an oily liquid, smelling like bitter almond oil, having a density of 1·023 at 0°, and boiling at 191°. It unites with the halogen-elements, the haloïd acids, and hydrogen.

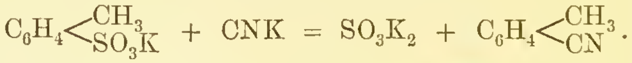
Substituted benzonitrils are obtained by dehydration of substituted benzamides, *e.g.*, $C_6H_4Br.CN$ by the action of phosphoric anhydride on bromobenzamide, $C_6H_4Br.CONH_2$.

Phenyl Isocyanide or **Phenyl-carbamine**, $C{\equiv}N{-}C_6H_5$, isomeric with benzonitril, is formed by distilling aniline with chloroform and alcoholic potash:

$$C_6H_5.NH_2 + CHCl_3 = 3HCl + C_6H_5{-}N{\equiv}C\,.$$

It is a liquid having a strong smell of prussic acid, and boiling, with partial decomposition, at 167°. It is dichroic; blue by reflected, green by transmitted light. It is not altered by alkalis, but acids convert it into aniline and formic acid. Heated to 200° it changes to benzonitril.

Cyanotoluene, $C_6H_4(CN).CH_3$. *Toluonitril.*—The three isomeric modifications of this compound are formed by treating the respective tolyl-sulphocarbimides, $N\left\{\begin{matrix}CS\\C_6H_4.CH_3\end{matrix}\right.$ with finely divided copper, which removes the sulphur, or by distilling the potassium salts of the corresponding toluenesulphonic acids with potassium cyanide:



$$C_6H_4{<}\begin{matrix}CH_3\\SO_3K\end{matrix} + CNK = SO_3K_2 + C_6H_4{<}\begin{matrix}CH_3\\CN\end{matrix}.$$

Ortho.—Colourless liquid, smelling like nitrobenzene, boiling at 203°–204°. *Para.*—Colourless needles, melting at 28·5°; boiling at 218°. *Meta.*—Not yet obtained in the pure state.

Benzyl Cyanide, $C_6H_5.CH_2.CN$, constitutes the principal part of the volatile oils of the garden nasturtium (*Tropæolum majus*), and of the garden cress (*Lepidium sativum*), and is produced artificially by heating benzyl chloride with alcohol and potassium cyanide. Colourless liquid boiling at 232°; specific gravity 1·0146 at 18°.

NITRO-DERIVATIVES.

These bodies are easily formed by the action of concentrated or fuming nitric acid on benzene and its homologues, the substitution of the NO_2-group for hydrogen taking place in the benzene-nucleus, never in the lateral chains; *e.g.*,

$$C_6H_5.CH_3 + NO_3H = C_6H_4(NO_2).CH_3 + H_2O\,.$$

On pouring the product into water, the nitro-compound separates out, generally in the form of a thick yellow or orange-coloured oil.

The more highly nitrated derivatives are most easily obtained by the action of a mixture of 1 part of strong nitric acid and 2 parts of strong sulphuric acid.

The aromatic nitro-compounds are mostly of a yellow colour; a few are liquid, the rest crystalline solids. By hydrogen sulphide or ammonium sulphide, and by stannous chloride, they are reduced to amido-compounds; by sodium-amalgam, or by heating with alcoholic potash, to azo-compounds (p. 465). They may also be converted into amido-compounds by heating with hydriodic acid:

$$\underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + 6HI = \underset{\text{Aniline.}}{C_6H_5NH_2} + 2H_2O + 3I_2 .$$

Nitrobenzenes.—Mononitrobenzene, $C_6H_5(NO_2)$, formed by gradually adding benzene to strong nitric acid in a cooled vessel, is a light yellow liquid, having an aromatic odour, boiling at 220°, solidifying at +3°. Sp. gr. 1·20 at 0.

Dinitrobenzenes, $C_6H_4(NO_2)_2$.—The three modifications are formed together by dropping benzene into a mixture of 2 vols. strong sulphuric and 1 vol. very strong nitric acid; and on crystallising the product from alcohol, the meta- compound, which constitutes by far the largest portion, separates out, while the other two remain in solution.

The *ortho-* compound, which forms the smallest portion of the product, crystallises from hot water in long needles, melting at 118°, soluble in 26 parts of alcohol at 24°, and in 3 parts of boiling alcohol.

The *meta*-compound (ordinary dinitrobenzene), forms long rhombic prisms melting at 89·8°, soluble in 17 parts of alcohol at 24°, and in all proportions of boiling alcohol.

The *para*-compound forms fan-shaped groups of monoclinic prisms, melting at 171°–172°, sparingly soluble in alcohol.

Trinitrobenzene, $C_6H_3(NO_2)_3$, formed by heating metadinitrobenzene with a mixture of pyrosulphuric acid (i. 212) and very strong nitric acid in sealed tubes, to 130°–140°, crystallises from alcohol in white laminæ or fern-like groups of needles. It melts at 121°–122°, dissolves sparingly in cold alcohol, easily in hot alcohol and in ether.

Nitro-haloid Derivatives of Benzene.—The action of nitric acid, or a mixture of nitric and sulphuric acids, on the chloro-, bromo-, and iodo-benzenes, gives rise to para- and ortho-mononitro-derivatives of the haloïd compounds, the former being always produced in greatest abundance. The same products are obtained from the corresponding nitranilines, $C_6H_4.NO_2.NH_2$, by exchange of the NH_2 for Cl, Br, or I, through the medium of the diazo-compounds. The meta-compounds are obtained in like manner from metanitraniline; metanitrochlorobenzene also by passing chlorine into nitrobenzene mixed with iodine, or better with $SbCl_3$.

The following are the melting and boiling points of the isomeric mononitro- chloro-, bromo-, and iodo-benzenes, $C_6H_4X(NO_2)$:

	Melting Points.			Boiling Points.		
	(1 : 2)	(1 : 3)	(1 : 4)	(1 : 2)	(1 : 3)	(1 : 4)
$C_6H_4Cl(NO_2)$	32·5°	44·4°	83°	243°	233°	242°
$C_6H_4Br(NO_2)$	41·5°	56°	126°	261°	256·5°	255–56
$C_6H_4I(NO_2)$	49·4°	36°	171°	...	280°	

These numbers show that the para-derivatives have the highest melting points, and the ortho-derivatives for the most part the lowest; the relations between the boiling points are less regular. The ortho- and para-compounds, heated in sealed tubes with aqueous potash, are converted into the corresponding phenols, $C_6H_4Cl.OH$, &c., whereas the meta-compounds do not exhibit this transformation.

Nitrodichloro- and *Nitrodibromobenzenes*, $C_6H_3Cl_2(NO_2)$, and $C_6H_3Br_2(NO_2)$.—These compounds are all crystalline, and melt at the temperatures shown in the following table:

$C_6H_3Cl_2(NO_2)$		$C_6H_3Br_2(NO_2)$	
1 : 2 : 4[*] . . .	32·2°	1 : 2 : 4 . . .	61·6°
1 : 2 : 5 . . .	55°	1 : 2 : 5 . . .	85·4°
1 : 3 : 5 . . .	65·4°	1 : 3 : 5 . . .	104·5°
1 : 3 : 4 . . .	43°	1 : 3 : 4 . . .	58·6°
		1 : 2 : 6 . . .	82·6°

Dinitrochlorobenzene, $C_6.Cl.NO_2.H.NO_2.H_2$, formed by treating either (1 : 2) or (1 : 4) chlorobenzene with a mixture of nitric and sulphuric acids, and from the corresponding dinitrophenol, $C_6H_3(NO_2)_2.OH$, by the action of PCl_5, crystallises in prisms melting at 53·4°. $C_6Cl.H.NO_2.NO_2.H_2$, formed in like manner from (1 : 3) nitrochlorobenzene, exhibits dimorphous modifications having different melting points (36·3°–38·8°).

Dinitrobromobenzene, $C_6H_3Br(NO_2)_2$, is known in two modifications analogous to the chlorine-compounds just described, and obtained in like manner. Both are crystalline; (1 : 2 : 4) melts at 75·3°; (1 : 3 : 4) at 59·4°.

Dinitroiodobenzene, $C_6.I.NO_2.H.NO_2.H_2$, from para- and ortho-iodonitrobenzene with nitrosulphuric acid, forms large yellow, transparent plates or prisms, melting at 88·5°.

Another modification, $C_6.I.NO_2.H.H.H.NO_2$, formed simultaneously with the last, crystallises in transparent orange-coloured rhombic tables, melting at 113·7°.

Trinitrochlorobenzene, $C_6.Cl.NO_2.H.NO_2H.NO_2$ (*Picryl chloride*), from picric acid, $C_6H_2(NO_2)_3.OH$ with PCl_5, forms needles melting at 83°. and like picric acid, forms crystalline compounds with many hydrocarbons.

[*] NO_2 in the position 1, in all the formulæ.

Nitrotoluenes.—*Para-* and *orthonitrotoluene*, $C_6H_4(NO_2).CH_3$, are formed by treating toluene with fuming nitric acid, and may be separated by fractional distillation. The former crystallises in nearly colourless prisms, melts at 54° and boils at 236°. The latter is a yellowish liquid boiling at 222°–223°.

Metanitrotoluene, obtained by the action of nitrous acid and alcohol on metanitroparatoluidine, $C_6.CH_3.H.NO_2.NH_2.H_2$, is crystalline, melts at 16°, and boils at 230°–231°.

Dinitrotoluene, $C_6.CH_3.NO_2.H.NO_2.H_2$, formed by treating toluene, or ortho- or para-nitrotoluene with nitro-sulphuric acid, crystallises in long colourless needles, melting at 70·5°. Another modification, obtained in like manner from metanitrotoluene, melts at 60°.

Trinitrotoluene, $C_6H_2(NO_2)_3.CH_3$, obtained by prolonged heating of a solution of toluene in nitrosulphuric acid, forms nearly colourless needles, slightly soluble in alcohol, melting at 82°.

Nitro-ethyl-benzenes, $C_6H_4(NO_2)—C_2H_5$ (*ortho-* and *para-*), are formed simultaneously by the action of fuming nitric acid on ethyl-benzene. Both are liquid, the former boiling at 227°–228°, the latter at 245°–246°. With tin and hydrochloric acid, they yield liquid bases, one of which, viz., *paramido-ethylbenzene*, $C_6H_4(NH_2).C_2H_5$, is also produced by heating the hydrochloride of ethylaniline to 300°–330°.

Nitroparaxylene, $C_6H_3(NO_2)(CH_3)_2$, is a pale yellow liquid which boils at 234°–237°, and does not solidify in a freezing mixture. —*Dinitroparaxylene*, $C_6H_2(NH_2)_2(CH_3)_2$. Two modifications of this compound are formed simultaneously by the action of fuming nitric acid on paraxylene, the less soluble in alcohol of the two forming long thin needles melting at 123·5°, while the other, which is more soluble in alcohol, forms large monoclinic crystals melting at 93°.

Trinitroparaxylene, $C_6H(NO_2)_3(CH_3)_2$, forms long, colourless needles, melting at 137°, moderately soluble in hot, sparingly in cold alcohol.

Nitromesitylene, $C_6H_2(NO_2)(CH_3)_3$, forms nearly colourless prisms, easily soluble in alcohol, melts at 42°, boils at 255°.—*Dinitromesitylene*, $C_6H(NO_2)_2(CH_3)_3$. Slender, colourless, brilliant needles, melting at 86°. *Trinitromesitylene*, $C_6(NO_2)_3(CH_3)_3$. Needles very slightly soluble in alcohol, melting at 232°.

Nitropseudocumene, $C_9H_{11}(NO_2)$, forms long needles, easily soluble in hot alcohol, melts at 71°, boils at 265°.—*Trinitropseudocumene*, $C_9H_9(NO_2)_3$. Colourless, quadratic prisms, melting at 185°

AMIDO-DERIVATIVES.

The replacement of hydrogen by NH_2 in the hydrocarbons homologous with benzene, gives rise to two series of metameric compounds, analogous to the haloïd and nitro-derivatives above described: thus, from toluene, $C_6H_5.CH_3$, are derived:

$C_6H_4(NH_2).CH_3$ Toluidine. $C_6H_5.CH_2(NH_2)$; Benzylamine.

and from xylene, $C_6H_4(CH_3)_2$:

$C_6H_3(NH_2).(CH_3)_2$ Xylidine.

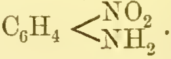
$C_6H_4<\begin{matrix}CH_3\\CH_2(NH_2)\end{matrix}$ Xylylamine.

These compounds are all of basic character; but those in which the NH_2 is situated in the lateral chains are stronger bases than their metamerides containing this group in the principal chain, and are analogous in their properties and their mode of formation to the amines of the fatty group; thus benzylamine, which may be represented by the formula $NH_2(C_7H_7)$, derived from ammonia by substitution of benzyl, C_7H_7, for hydrogen, is formed, together with dibenzylamine, $NH(C_7H_7)_2$, and tribenzylamine, $N(C_7H_7)_3$, by heating benzyl chloride with ammonia, just as ethylamine is formed from the chloride, bromide, or iodide of ethyl. Toluidine and its homologues, on the other hand, are produced chiefly by the action of reducing agents on the nitro-derivatives; and amidobenzene, aniline, or phenylamine, $C_6H_5—NH_2$, which may be regarded as the first term of either series, is formed for the most part in the same manner.

The reduction of the nitro-derivatives is effected:

1. By the action of ammonium sulphide in alcoholic solution:

$$C_6H_5.NO_2 + 3H_2S = C_6H_5.NH_2 + 2H_2O + 3S.$$

In the application of this method to di- and tri-nitro-compounds, only one nitro-group is reduced in the first instance, so that nitro-amido compounds are obtained, such as  $C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix}$.

2. By the action of zinc or tin and hydrochloric acid, or of iron filings and acetic acid. In these cases, the reduction may be supposed to be effected by nascent hydrogen:

$$C_6H_5.NO_2 + 3H_2 = C_6H_5.NH_2 + 2H_2O;$$

in the case of iron and acetic acid, also through the intervention of the ferrous salt formed in the first instance:

$$C_6H_5.NO_2 + 6FeO + H_2O = C_6H_5.NH_2 + 3Fe_2O_3,$$

and in that of tin and hydrochloric acid, through the intervention of stannous chloride:

$$C_6H_5.NO_2 + 3Sn + 6HCl = C_6H_5.NH_2 + 3SnCl_2 + 2H_2O$$

and

$$C_6H_5.NO_2 + 3SnCl_2 + 6HCl = C_6H_5.NH_2 + 3SnCl_4 + 2H_2O.$$

To effect this last reaction, the nitro-compound is drenched with fuming hydrochloric acid, and the calculated quantity of granulated tin is gradually added. The action usually begins after a while, without application of heat, the tin and the nitro-compound dissolving. From the warm solution, which contains a double salt, consisting of the hydrochloride of the resulting base combined with stannic chloride, *e.g.* $(C_6H_5.NH_2.HCl)_2.SnCl_4$, the tin is precipitated by hydrogen sulphide, and the stannic sulphide is separated by filtration, leaving the hydrochloride of the amido-compound in solution.

When a di- or a tri-nitro-compound is thus treated, all the nitro-groups are usually reduced at once: hence this process is especially applicable to the preparation of di- and tri-amido-derivatives. If, however, only half the calculated quantity of tin be added, a partial reduction may be effected, and nitro-amido-compounds obtained.

Amidobenzenes.

Aniline, $C_6H_7N = C_6H_5.NH_2$ — *Phlenylamine.* — This base, which is now prepared in enormous quantities for the manufacture of colouring matters, was discovered in 1826 by Unverdorben, who obtained it by the dry distillation of indigo. Fritzsche, in 1841, found that it might be obtained by boiling indigo with potash-ley; and Zinin, about the same time, introduced the method of preparing it by reduction of nitrobenzene with ammonium sulphide,—a process which, as already observed, is very generally applicable to the preparation of organic bases.

To prepare aniline in this way, an alcoholic solution of nitrobenzene is mixed with ammonia, and gaseous hydrogen sulphide is passed into the liquid as long as sulphur continues to be precipitated: the reaction is greatly accelerated by warming the liquid. The solution is then mixed with excess of acid, filtered to separate the sulphur, boiled to expel alcohol and excess of nitrobenzene, and then distilled with excess of potash.

On the large scale, aniline is prepared by reducing nitrobenzene with ferrous acetate. Nitrobenzene (1 part) is heated with iron filings (1½ part), and glacial acetic acid (1 part), and the solid product of the reaction is mixed with lime, and distilled with superheated steam. On the small scale, the best results are obtained by reduction with tin and hydrochloric acid. The product obtained by either process may be purified by converting it into oxalate, crystallising this salt several times from alcohol, and decomposing it with potash.

Aniline is also produced by heating phenol with ammonium chloride and fuming hydrochloric acid in sealed tubes to 315° for about thirty hours:

$$C_6H_5.OH + NH_3 = C_6H_5.NH_2 + H_2O;$$

and lastly, it is formed by the destructive distillation of nitrogenous organic matters, and is one of the constituents of coal-tar oil.

Aniline is a colourless oily liquid, having a faint peculiar odour, a density of 1·036 at 0°, and boiling at 184·5°. When quite pure it solidifies at low temperatures, and melts at −8°. It dissolves but sparingly in water (in 31 parts at 12°), easily in alcohol and ether. When exposed to the air it turns brown and gradually resinises. Its aqueous solution, mixed with chloride of lime, assumes a purple-violet colour. Its solution in strong sulphuric acid acquires, on addition of a few drops of aqueous potassium dichromate, first a red, then a deep blue colour. A deal shaving dipped into aniline is coloured yellow.

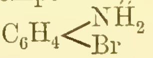
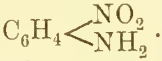
Aniline is a strong base, uniting directly with acids and with certain salts, forming, for example, the compounds $(C_6H_7N)_2.SnCl_2$ and $(C_6H_7N)_2.CuSO_4$. — The *hydrochloride*, $C_6H_7N.HCl$, forms needles very soluble in water and in alcohol, subliming without decomposition. Its alcoholic solution, mixed with platinic chloride, deposits the *platinochloride*, $(C_6H_7N.HCl)_2.PtCl_4$, in yellow needles. The *nitrate*, $C_6H_7N.NO_3H$, crystallises in large rhombic tables; the *oxalate*, $(C_6H_7N)_2.C_2O_4H_2$, separates from a mixture of the alcoholic solutions of aniline and oxalic acid, in rhombic prisms.

SUBSTITUTION-PRODUCTS OF ANILINE.

1. *Halogen-Derivatives.*—These compounds are formed :

(1.) By the action of halogen-elements on aniline, bromine and chlorine forming di- or tri-derivatives, iodine giving rise to para-iodaniline. The monochlor- and mono-bromanilines (para) are obtained by the action of chlorine and bromine, in vapour or in aqueous solution, on acetanilide, $C_6H_5.NH(C_2H_3O)$, suspended in water.

(2.) By reduction of the nitrochloro-, nitrobromo- or nitroiodo-benzenes with ammonium sulphide, or with tin and hydrochloric acid, $C_6H_4Cl(NO_2)$, for example, being thus converted into $C_6H_4Cl(NH_2)$.

(3.) From the nitranilines by substitution of Cl, Br, or I for NH_2 (through the medium of the diazo-compounds), and of NH_2 for NO_2 by the action of reducing agents,  $C_6H_4{<}^{NH_2}_{Br}$ for example from  $C_6H_4{<}^{NO_2}_{NH_2}$.

By the entrance of halogen-elements (also of the nitro-group) into the molecule, the basic properties of aniline are weakened. The monoderivatives are weak bases; the di-derivatives form, for the most part, very unstable salts which are decomposed even by water; and the tri-derivatives are mostly destitute of basic properties, though the orientation of the substituted radicles has some influence in this respect. In the mono-derivatives, the ortho-compounds are less basic than the meta- and para-compounds.

The following table exhibits the modes of formation and the chief physical properties of the halogen-derivatives of aniline:

	Formation.	Physical character at ordinary temperatures.	Melting Point.	Boiling Point.
loranilines.				
o- $C_6H_4Cl(NH_2)$				
rtho (1:2)	from 1:2 $C_6H_4Cl(NO_2)$	Liquid: sp. gr. 1·2338 at 0°	−14°	207°
eta (1:3)	1:3 ,,	Liquid; sp. gr, 1·2432 at 0°	—	230°
ra (1:4)	1:4 ,,	Rhombic crystals	70-71°	230-231°
$C_6H_3Cl_2(NH_2)$				
1:2:4*	from dichloracetanilide and dichlorisatin by potash	Flat flexible needles	63°	245°
1:2:5	from 1:2:5 $C_6H_4Cl_2(NO_2)$	Colourless needles	50°	
1:3:5	,. 1;3;5 ,,	Long needles	50·5°	
1:3:4	,, 1:3:4	Crystalline	71·5°	272°
$C_6H_2Cl_3(NH_2)$				
1:2:4:6	from aniline with Cl, best in acetic acid solution	Long colourless needles: non-basic	77·5°	260°
1:2:4:5	from $C_6H_2Cl_3(NO_2)$	Colourless needles	96·5	270°
omanilines.				
o-$C_6H_4Br(NH_2)$				
tho (1:2)	from 1:2 $C_6H_4Br(NO_2)$	Colourless needles; insol. in water, very sol. in alcohol	31·5°	229°
ta (1:3)	,, 1:3 ,,	Crystalline mass	18-18·5°	251°
ra (1:4)	,, 1:4 ,,	Large rhombic crystals, looking like regular octohedrons	64°	Decomposed by distillation into aniline, 1:2:4 di-, and 1:2:4:6 tri-brom-aniline.
$_6H_3Br_2(NH_2)$				
1:2:4	from aniline with Br: from dibromacetanilide with alkalis; from 1:2:5, $C_6H_3Br_2(NO_2)$, by reduction; from $C_6H_5NO_2$, by heating with conc. HBr to 185°-190° (together with mono- and tribromaniline), and by distilling dibromisatin with potash.	Colourless shining needles	79·5°	
1:2:5	from 1:2:5 $C_6H_3Br_2(NO_2)$	Warty groups of silky prisms	51-52°	
1:3:5	,, 1:3:5 ,,	White needles	56·4°	
1:3:4	,, 1:3:4 ,,	Colourless needles; this and 1:3:5 are more basic than the two former	80·4°	
$C_6H_2Br_3(NH_2)$				
1;2:4:6	from aniline, para-, and ortho-bromaniline, with excess of Br, and by reduction of 1:2:4:6 $C_6H_2Br_3(NO_2)$	Long colourless needles: non-basic	119·6	
1:3:4:5	from 1:3:4:5 $C_6H_2Br_3(NO_2)$	Crystalline: unites with acids	Does not melt at 130°	
- $C_6HBr_4(NH_2)$				
1:2:3:4;6	from 1:3 bromaniline and 1:2:5 di-bromaniline with excess of bromine	Fine long silky needles	115·3°	
- $C_6Br_3(NH_2)$	from 1:3:5 di-bromaniline with Br	Large needles	Does not melt at 222°	
danilines.				
$C_6H_4I.NH_2$(1:3)	from 1:3 $C_6H_4I(NO_2)$	Silvery laminæ	25°	
,, (1:4)	,, 1:4 ,,	Colourless needles	60°	

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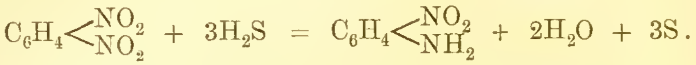
* NH_2 in position 1 throughout.

2. *Nitro-derivatives.*

Mononitranilines, $C_6H_4(NO_2).NH_2$.—The three isomeric derivatives are formed by imperfect reduction of the dinitrobenzenes (p. 443), best by passing hydrogen sulphide into the alcoholic solution of the nitro-compound, mixed with a little concentrated ammonia:



$$C_6H_4<{}^{NO_2}_{NO_2} + 3H_2S = C_6H_4<{}^{NO_2}_{NH_2} + 2H_2O + 3S.$$

The ortho- and para-derivatives are also formed by the action of alkalis on the corresponding nitro-acetanilides, $C_6H_5.NH(C_2H_3O)$, and by prolonged heating of ortho- and para-nitrobromobenzene, or of the methylic ether of ortho- or para-nitrophenol, with aqueous or alcoholic ammonia to 180–200°:

$$C_6H_4(NO_2)Br + NH_3 = HBr + C_6H_4(NO_2)(NH_2).$$

$$C_6H_4(NO_2)(OCH_3) + NH_3 = HOCH_3 + C_6H_4(NO_2)(NH_2).$$

Nitranisol. Methyl alcohol. Nitraniline.

Ortho-nitraniline forms long, dark yellow needles, melting at 71·5°, more soluble in water and in alcohol than the other two modifications. *Meta*—Long yellow prisms, melting at 109°, slightly soluble in water, freely in alcohol. *Para*—Orange-coloured needles or tables, melting at 146°, nearly insoluble in water, easily soluble in alcohol.

Dinitranilines, $C_6H_3(NO_2)_2NH_2$.—The unsymmetrical modification 1 : 2 : 4 (NH_2 in 1), is formed by heating the corresponding dinitro-, chloro-, bromo-, or iodo-benzene, or the methylic ether of (1 : 2 : 4) dinitrophenol with alcoholic ammonia, or dinitro-acetanilide with potash-ley. It crystallises in light yellow prisms, melting at 182°–183°; does not combine with acids. By exchange of NH_2 for H it is converted into meta-dinitrobenzene.

Consecutive Dinitraniline (1 : 2 : 6), from the corresponding dinitro-iodobenzene or methyl-dinitrophenol, forms long, dark yellow needles, melting at 138°, sparingly soluble even in hot alcohol.

Trinitraniline, $C_6H_2(NO_2)_3.NH_2$ (1 : 2 : 4 : 6) *(Picramide)*, is formed by the action of alcoholic ammonia on trinitrochlorobenzene, $C_6.Cl.NO_2.H.NO_2H.NO_2$ (p. 444), or on the ethylic or methylic ether of picric acid. It crystallises from alcohol in orange-red needles; from glacial acetic acid in large monoclinic tables; melts at 186°. By heating with alkalis it is converted into a salt of picric acid:

$$C_6H_2(NO_3)_3.NH_2 + KOH = NH_3 + C_6H_2(NO_2)_3OK.$$

Chloro- and Bromo-nitranilines, of which numerous modifications are known, are obtained by heating nitrodichloro- and nitrodibromo-benzenes with alcoholic ammonia; by treating chlor-

and brom-acetanilides with nitric acid, and decomposing the resulting nitro-compounds with alkalis; and by passing chlorine gas or bromine vapour into the solution of the three nitranilines in hydrochloric acid.

Diamidobenzenes or **Phenylenediamines**, $C_6H_4(NH_2)_2$.—These bases are formed by reduction of the three dinitrobenzenes or the three nitranilines with tin and hydrochloric acid; also by dry distillation of the corresponding diamidobenzoic acids. They are bi-acid bases, forming well-defined crystalline salts; *e.g.*, $C_6H_4(NH_2)_2.2HCl$.

Ortho—Colourless or slightly reddish four-sided tables; melts at 102°; boils at 252°; dissolves in water, especially when hot. Its solution in hydrochloric acid is coloured dark red by ferric chloride or potassium dichromate. *Meta*—Crystalline mass, easily soluble in water; melts at 63°, boils at 287°. *Para*—Colourless, or faintly reddish scales, easily soluble in water; melts at 147°, boils at 267°.

Triamidobenzene, $C_6H_3(NH_2)_3$ (1:2:4), is produced by dry distillation of triamidobenzoic acid mixed with pounded glass, and by reduction of (1:2:4) dinitraniline with tin and hydrochloric acid. It forms a dark red radio-crystalline mass, melting at 103°, boiling at 330°; easily soluble in water, alcohol, and ether; separated from its aqueous solution by caustic soda. By ferric chloride and by strong sulphuric acid containing a little nitric acid, its solution is coloured deep blue. It forms well-defined salts with acids.

ALCOHOLIC DERIVATIVES OF ANILINE.

The partial or total replacement of the hydrogen in the amidogen-group of aniline by alcohol-radicles, gives rise to compounds analogous to the secondary and tertiary amines of the fatty group, and formed in like manner by heating aniline with the iodides and bromides of the alcohol-radicles; *e.g.*,

$$\underset{\text{Aniline.}}{C_6H_5NH_2} + CH_3Br = HBr + \underset{\text{Methyl-aniline.}}{C_6H_5.NH.CH_3}.$$

They may also be produced by heating aniline hydrochloride with alcohols in closed vessels, a chloride of the alcohol-radicle being first formed, which then acts as above on the aniline. The tertiary derivatives, such as diethylaniline, $C_6H_5N(C_2H_5)_2$, can also unite with alcoholic iodides, forming ammonium compounds, like methyl-diethyl-phenylammonium, $(CH_3)(C_2H_5)_2(C_6H_5)NI$, which, when treated with moist silver oxide, yield the corresponding hydroxides, such as $(CH_3)(C_2H_5)_2(C_6H_5)N.OH$. These hydroxides are very soluble in water, strongly alkaline, and have a bitter taste.

The secondary and tertiary derivatives are liquid at ordinary temperatures, and exhibit the following physical properties:

		Boiling Point.	Specific Gravity.
Methylaniline,	$C_6H_5NH(CH_3)$	190–191°	0·976 at 15°
Dimethylaniline,	$C_6H_5N(CH_3)_2$	192°	0·9553 at 15°
Ethylaniline,	$C_6H_5NH(C_2H_5)$	204°	0·954 at 18°
Diethylaniline,	$C_6H_5N(C_2H_5)_2$	213·5°	0·939 at 18°
Amylaniline,	$C_6H_5NH(C_5H_{11})$	258°	
Amyl-ethylaniline,	$(C_6H_5)N(C_2H_5)(C_5H_{11})$	262°	

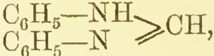
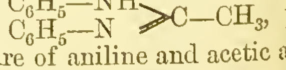
Dimethylaniline solidifies at +0·5°. Amylethyl-aniline unites with methyl iodide, forming the iodide of methylethylamylphenyl-ammonium $(C_6H_5)N(CH_3)(C_2H_5)(C_5H_{11})$.

Many other alcoholic derivatives of aniline have been prepared and examined.

Diphenylamine, $NH(C_6H_5)_2$, is formed by heating aniline hydrochloride with aniline to 240°, and by the dry distillation of triphenyl-rosaniline (aniline blue). It is a crystalline body, having a pleasant odour, melting at 54°, and boiling at 310°; slightly soluble in water, easily in alcohol and ether; coloured deep blue by nitric acid. It is a weak base, its salts being decomposed by water.

Triphenylamine, $N(C_6H_5)_3$, is produced, together with diphenylamine, by heating a solution of potassium in aniline with monobromobenzene.

Derivatives containing diatomic alcohol-radicles are formed by heating aniline with the iodides or bromides of methene and ethene. *Methene-diphenyldiamine*, $(C_6H_5.NH)_2.CH_2$, is viscid and uncrystallisable. *Ethene-diphenyldiamine*, $(C_6H_5.NH)_2.C_2H_4$, is crystalline, and melts at 57°. The isomeric *ethidene-diphenyldiamine*, $(C_6H_5.NH)_2.CH—CH_3$, formed by the action of aldehyde on aniline, separates from alcoholic solution in yellowish nodules.

Derivatives containing tri-atomic alcohol radicles are obtained by heating aniline with the chlorides of such radicles, or with substances capable of forming them. *Methenyl-diphenylamine*,  $\left.\begin{matrix}C_6H_5\text{—}NH\\C_6H_5\text{—}N\end{matrix}\right\rangle CH$, produced by heating aniline with chloroform to 180°–190°, or by the action of phosphorus trichloride on a mixture of aniline and formanilide, crystallises in long colourless needles, melting at 135°–136°, and boiling, with partial decomposition, above 250°. *Ethenyl-diphenyldiamine*,  $\left.\begin{matrix}C_6H_5\text{—}NH\\C_6H_5\text{—}N\end{matrix}\right\rangle C\text{—}CH_3$, produced by the action of PCl_3 on a mixture of aniline and acetic acid, forms small colourless needles melting at 131°–132°.

DERIVATIVES CONTAINING ACID RADICLES :—ANILIDES.

These compounds, which may be regarded as amides having their hydrogen more or less replaced by phenyl, are formed: 1. By the action of acid chlorides or chloranhydrides on aniline; thus:

$$\underset{\text{Aniline.}}{C_6H_5.NH_2} + \underset{\text{Acetic chloride.}}{C_2H_3O.Cl} = HCl + \underset{\text{Acetanilide.}}{C_6H_5.NH_2.C_2H_3O}.$$

2. By heating aniline salts with organic acids:

$$C_6H_5.NH_2 + C_2H_3O.OH = H_2O + C_6H_5.NH.C_2H_3O.$$

By heating with alkalis, or with hydrochloric acid, they are resolved into their components; *e.g.*,

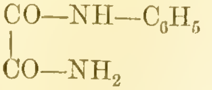
$$C_6H_5.NH.C_2H_3O + KOH = C_2H_3O.OK + C_6H_5.NH_2.$$

Formanilide, $C_6H_5.NH.CHO$—*Phenylformamide.*—Produced by heating aniline with ethyl formate, or, together with other products, by quickly heating it with oxalic acid:

$$C_6H_5.NH_2 + C_2O_4H_2 = C_6H_5.NH.CHO + CO_2 + H_2O.$$

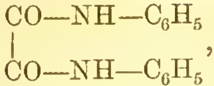
It forms prisms, melting at 46°, easily soluble in water, alcohol, and ether. Strong soda-ley added to its aqueous solution throws down sodium formanilide, $C_6H_5.NNa—CHO$, which is resolved by water into formanilide and sodium hydroxide. By distillation with strong hydrochloric acid, it yields a small quantity of benzonitril: $C_6H_5.NH.CHO = C_6H_5.CN + H_2O$.

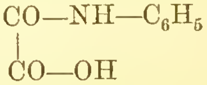
Acetanilide, $C_6H_5.NH.C_2H_3O$, *Phenylacetamide*, produced by heating aniline and glacial acetic acid (1 mol. of each) for several hours, or by the action of acetyl chloride or acetic anhydride on aniline, forms colourless, shining laminar crystals, melting at 112°–113°, volatilising without decomposition at 295°, sparingly soluble in cold water, more easily in hot water and in alcohol. Treated with bromine, chlorine, or nitric acid, it yields mono- and di-substitution products, the substitution always taking place in the benzene-ring, and these when heated with alkalis yield alcoholic anilines. *Monobromacetanilide*, $C_6H_4Br-NH(C_2H_3O)$ (1:4), melts at 165°; *dibromacetanilide* at 146°; *paranitracetanilide* melts at 207°; *ortho-* at 78°. *Dinitracetanilide*, $C_6H_3(NO_2)_2.NH(C_2H_3O)$, formed by dissolving acetanilide in a mixture of nitric and sulphuric acids, melts at 120°.



$$\begin{array}{l} CO—NH—C_6H_5 \\ | \\ CO—NH_2 \end{array}$$

Oxanilamide, , *Phenyloxamide*, formed, together with oxanilide, by evaporating cyananiline (p. 458) with hydrochloric acid, crystallises in laminæ, soluble in hot water, and subliming without decomposition.

Oxanilide,  $\begin{matrix}CO—NH—C_6H_5\\ |\\ CO—NH—C_6H_5\end{matrix}$, *Diphenyloxamide,* obtained by heating aniline oxalate to 160°–180°, and together with oxanilamide, by evaporating a solution of cyananiline in hydrochloric acid, forms shining sublimable crystals, melting at 245°.

Oxanilic Acid,  $\begin{matrix}CO—NH—C_6H_5\\ |\\ CO—OH\end{matrix}$, produced by heating aniline with excess of oxalic acid, forms crystalline scales slightly soluble in cold, easily in hot water, and having a strong acid reaction. It is monobasic.

Carbanilamide, $CO{<}\begin{matrix}NH—C_6H_5\\ NH_2\end{matrix}$, *Phenyl-carbamide, Phenyl-urea,* is formed, like ethyl-carbamide (p. 396), by passing cyanic acid vapour into aniline, and by the action of ammonia on phenyl isocyanate (carbanil):

$$CO{=}N—C_6H_5 + NH_3 = CO{<}\begin{matrix}NH—C_6H_5\\ NH_2\end{matrix}.$$

The easiest method of preparing it is to evaporate an aqueous solution of potassium cyanide and aniline sulphate. It forms colourless, needle-shaped crystals, melting at 144°–145°, sparingly soluble in cold water, easily in hot water, and in alcohol and ether. Decomposed by heat into ammonia, cyanuric acid and carbanilide.

Alcoholic derivatives of phenylcarbamide, *e.g., ethyl-phenyl-carbamide,* $CO{<}\begin{matrix}NH.C_6H_5\\ NH.C_2H_5\end{matrix}$, are formed by the action of aniline on isocyanic ethers (carbimides, p. 98).

Carbanilide, $CO{<}\begin{matrix}NH.C_6H_5\\ NH.C_6H_5\end{matrix}$, *Diphenyl-carbamide, Diphenyl-urea* (symmetrical), is produced by the action of carbonyl chloride (phosgene) on aniline :

$$COCl_2 + 2(C_6H_5.NH_2) = 2HCl + CO(NH.C_6H_5)_2 ;$$

by combination of phenyl isocyanate (carbanil) with aniline :

$$CO{=}N—C_6H_5 + NH_2.C_6H_5 = CO(NH.C_6H_5)_2 ;$$

by heating 1 part of urea with 3 parts of aniline to 150°–170°:

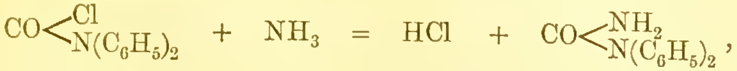
$$CO(NH_2)_2 + 2(C_6H_5.NH_2) = 2NH_3 + CO(NH.C_6H_5)_2 ;$$

also by heating 1 mol. aniline with 1 mol. carbanilamide ; and, together with formanilide, by the action of heat on oxanilamide. It forms silky needles, slightly soluble in water, moderately soluble in alcohol, melts at 235°, and volatilises without decomposition.

Chlorocarbanilide, $COCl—N(C_6H_5)_2$, is formed by passing phosgene gas into a solution of diphenylamine in chloroform :

$$COCl_2 + NH(C_6H_5)_2 = HCl + COCl—N(C_6H_5)_2 .$$

It crystallises in colourless laminæ. With alcoholic ammonia it forms unsymmetrical diphenyl-carbamide :



$$CO<\begin{array}{l}Cl\\N(C_6H_5)_2\end{array} + NH_3 = HCl + CO<\begin{array}{l}NH_2\\N(C_6H_5)_2\end{array},$$

which crystallises in long needles melting at 189°. Heated with aniline, it yields triphenyl-carbamide, $CO<\begin{array}{l}NH.C_6H_5\\N(C_6H_5)_2\end{array}$ (needles melting at 136°); and with diphenylamine at 200°–220° it forms tetraphenyl carbamide, $CO[N(C_5H_5)_2]_2$, light yellow crystals, melting at 183°.

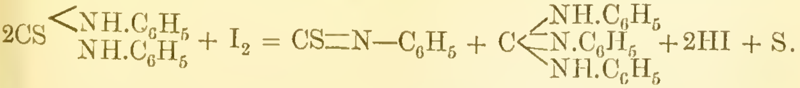
Carbanilic or **Phenylcarbamic Acid,** $CO<\begin{array}{l}NH.C_6H_5\\OH\end{array}$, is not known in the free state. Its ethers, the phenylurethanes, are formed by the action of alcohols on carbanil. The *ethylic ether*, $CO<\begin{array}{l}NH.C_6H_5\\OC_2H_5\end{array}$, produced also by the action of ethyl chlorocarbonate, $COCl.OC_2H_5$, on aniline, forms colourless needles melting at 52°. It boils at 237°–238°, with partial decomposition into alcohol and carbanil, and is converted, by heating with strong potash-ley, or with aniline, into diphenylcarbamide.

Carbanil, Phenyl Isocyanate or **Phenyl-carbimide,** $CO{=}N{-}C_6H_5$, formed by distilling oxanilide, or better ethylic carbanilate, with phosphoric anhydride, is a mobile liquid, boiling at 163°, and having a pungent, tear-exciting odour. Its reactions are exactly like those of the isocyanic ethers already described (p. 104). With water it forms carbanilide :

$$2(CO{=}N{-}C_6H_5) + H_2O = CO_2 + CO(NH.C_6H_5)_2.$$

By ammonia it is converted into carbanilamide, and by amines into alcoholic derivatives of that compound. It unites with alcohols to form the carbanilic ethers.

Thiocarbanil or **Phenyl-thiocarbimide,** $CS{=}N{-}C_6H_5$, also called *Phenylic Mustard-oil*, is formed from thiocarbanilide by distillation with phosphoric anhydride, by prolonged boiling with hydrochloric acid, and, together with triphenylguanidine, by the action of iodine in alcoholic solution:



$$2CS<\begin{array}{l}NH.C_6H_5\\NH.C_6H_5\end{array} + I_2 = CS{=}N{-}C_6H_5 + C\begin{array}{l}\diagup NH.C_6H_5\\\leftarrow N.C_6H_5\\\diagdown NH.C_6H_5\end{array} + 2HI + S.$$

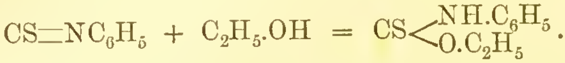
It is also produced by the action of phosgene on aniline. It is a colourless liquid, smelling like mustard-oil, boiling at 222°. By heating with reduced copper it is converted into phenyl cyanide benzonitril):

$$CS{=}N{-}C_6H_5 + Cu = CuS + CN.C_6H_5.$$

Hydrogen sulphide passed into phenyl-thiocarbimide decomposes it, even at ordinary temperatures, into thiocarbanilide and carbon disulphide:

$$2(CS{=}N.C_6H_5) + SH_2 = CS_2 + CS(NH.C_6H_5)_2.$$

It unites with ammonia to form phenylthiocarbamide; with aniline, to form diphenylcarbamide; and with anhydrous alcohol at 120°, to form phenylic thiocarbamates or thiourethanes:

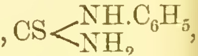


$$CS{=}NC_6H_5 + C_2H_5.OH = CS{<}{\substack{NH.C_6H_5\\ O.C_2H_5}}.$$

Normal Phenyl Thiocyanate, $CN.S.C_6H_5$, isomeric with thiocarbanil, is obtained by the action of cyanogen chloride on the lead-salt of phenyl-mercaptan:

$$(C_6H_5S)_2Pb + 2CNCl = PbCl_2 + 2(CN.S.C_6H_5).$$

It is a colourless liquid which boils at 231°, and reacts like the normal thiocyanic ethers of the fatty series.



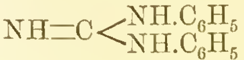
Thiocarbanilamide or **Phenylthiocarbamide,** $CS{<}{\substack{NH.C_6H_5\\ NH_2}}$, formed by the combination of ammonia with thiocarbanil, crystallises in needles, melting at 154°, slightly soluble in cold, more easily in boiling water and in alcohol. When boiled with silver nitrate it exchanges its sulphur for oxygen, and is converted into phenylcarbamide.

Thiocarbanilide or **Diphenylthiocarbamide,** $CS(NH.C_6H_5)_2$, is formed by the action of carbon disulphide on aniline:

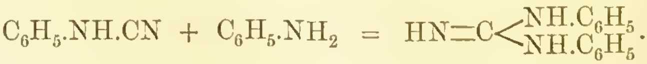
$$2NH_2C_6H_5 + CS = SH_2 + CS(NH.C_6H_5)_2.$$

Aniline and potassium hydroxide, in equal numbers of molecules, are heated for an hour in alcoholic solution with excess of carbon sulphide; the resulting liquid is poured into dilute hydrochloric acid; the alcohol evaporated; and the mass crystallised from alcohol.

Thiocarbanilide forms colourless laminæ melting at 144°, insoluble in water, easily soluble in alcohol and ether. The mode of its conversion into phenyl-thiocarbimide and triphenyl-guanidine has been already explained (p. 455). By treating it with alcoholic ammonia and lead oxide the S is replaced by NH, and diphenyl-guanidine is produced.



Diphenyl-guanidine, $NH{=}C{<}{\substack{NH.C_6H_5\\ NH.C_6H_5}}$ (*Melaniline*), is also formed by the action of gaseous cyanogen chloride on dry aniline, and by boiling cyananilide with aniline hydrochloride:



$$C_6H_5.NH.CN + C_6H_5.NH_2 = HN{=}C{<}{\substack{NH.C_6H_5\\ NH.C_6H_5}}.$$

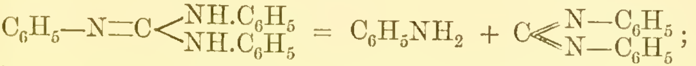
It forms long flattened needles, melting at 147°, soluble in 10 parts of alcohol at ordinary temperatures, slightly soluble in water. It is a mono-acid base, and forms well-crystallised salts. When heated above its melting-point, it is resolved into ammonia, aniline, and *tetraphenyl-melamine*, $C_3N_6H_2(C_6H_5)_4$. By carbon disulphide it is converted into thiocarbanilide and thiocyanic acid:

$$HN{=}C(NH.C_6H_5)_2 + CS_2 = CS(NH.C_6H_5)_2 + CNSH.$$

Triphenyl-guanidine (α), $C_6H_5{-}N{=}C{<}\begin{matrix}NH.C_6H_5\\ NH.C_6H_5\end{matrix}$, is formed by the action of heat on diphenyl-carbamide; by heating diphenyl-thiocarbamide either alone or with copper to 150°–160°, or with aniline to the boiling point of the latter. It is most easily prepared by heating an alcoholic solution of diphenyl-thiocarbamide and aniline with lead oxide or mercuric oxide, or with an alcoholic solution of aniline to the boiling point:

$$CS(NH.C_6H_5)_2 + C_6H_5.NH_2 = SH_2 + C_6H_5{-}N{=}C(NH.C_6H_5)_2.$$

Triphenyl-guanidine crystallises in shining rhombic prisms, melting at 143°, nearly insoluble in water even at the boiling heat, easily soluble in hot alcohol. It is a mono-acid base, forming well-crystallised salts. By distillation it is resolved into aniline and diphenyl-cyanamide or carbodiphenylimide, which recombine in the receiver:

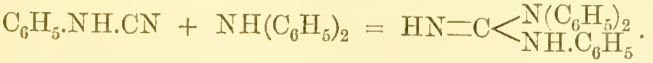


$$C_6H_5{-}N{=}C{<}\begin{matrix}NH.C_6H_5\\ NH.C_6H_5\end{matrix} = C_6H_5NH_2 + C{\ll}\begin{matrix}N{-}C_6H_5\\ N{-}C_6H_5\end{matrix};$$

and by heating to 160°–170° with carbon disulphide, into phenyl-thiocarbamide and diphenyl-thiocarbamide:

$$C_6H_5N{=}C(NH.C_6H_5)_2 + CS_2 = CS{=}N.C_6H_5 + CS(NH.C_6H_5)_2.$$

An isomeric *triphenyl-guanidine* (β), $HN{=}C{<}\begin{matrix}N(C_6H_5)_2\\ NH.C_6H_5\end{matrix}$, is formed by heating cyananilide with diphenylamine hydrochloride:

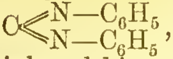


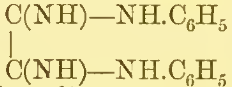
$$C_6H_5.NH.CN + NH(C_6H_5)_2 = HN{=}C{<}\begin{matrix}N(C_6H_5)_2\\ NH.C_6H_5\end{matrix}.$$

It crystallises in large tables melting at 131°.

Tetraphenyl-guanidine, $HN{=}C[N(C_6H_5)_2]_2$.—The hydrochloride is formed by passing gaseous cyanogen chloride into fused diphenylamine heated to 160°–170°. The free base separated therefrom by an alkali forms colourless rhombic prisms, melting at 130°–131°.

Phenyl-cyanamide, or **Cyananilide**, $CN.NH.C_6H_5$, formed by passing gaseous cyanogen chloride into an ethereal solution of dry aniline, or by digesting an alcoholic solution of phenyl-thiocarbamide with lead oxide, crystallises in long needles, melting at 36°–37°, sparingly soluble in water, easily in alcohol and ether. It has no basic properties, but unites with hydrogen sulphide to form phenylthiocarbamide, $NH_2.CS.NH(C_6H_5)$, and is converted spontaneously, even at ordinary temperatures, into the polymeric compound triphenyl-melamine, $C_3N_6H_3(C_6H_5)_3$, which crystallises in prisms melting at 162°–163°.

Diphenylcyanamide or **Carbo - diphenylimide,** $C_{13}H_{16}N_2$ =  $C\ll\begin{smallmatrix}N-C_6H_5\\N-C_6H_5\end{smallmatrix}$, is formed by adding mercuric oxide to a solution of diphenylthiocarbamide in hot benzene, and, together with aniline, by distillation of α-triphenyl-guanidine. It is a syrupy liquid, boiling at 330°–331°, and changing, when kept in an exsiccator, into a solid polymeric compound. Hydrochloric acid gas passed into its solution in hot benzene converts it into a crystalline hydrochloride, $C_{13}H_{10}N_2.HCl$. By boiling with aqueous alcohol it is converted into diphenylcarbamide. It unites with SH_2 to form diphenylthiocarbamide, and with CS_2 at 140°–150° to form phenylthiocarbimide, $C(N.C_6H_5)_2 + CS_2 = 2(CS=N-C_6H_5)$.

Cyananiline, $(C_6H_5.NH_2)_2(CN)_2$ =  $\begin{matrix}C(NH)-NH.C_6H_5\\|\\C(NH)-NH.C_6H_5\end{matrix}$, separates on passing cyanogen gas into an alcoholic solution of aniline, in shining laminæ, melting at 210°. It is a biacid base, and is resolved by boiling with acids into oxamide and oxanilide.

PHENYL PHOSPHORUS-COMPOUNDS.

Phosphenyl Chloride, $C_6H_5.PCl_2$, formed by repeatedly passing a mixture of the vapours of benzene and phosphorus trichloride through a red-hot tube filled with fragments of pumice, and in small quantity by heating mercury-diphenyl with phosphorus trichloride, is a fuming, strongly refracting liquid, having a density of 1·319 at 20°, and boiling at 222° ; decomposed by water into hydrochloric and phosphenylous acids. It unites with *chlorine*, forming the tetrachloride, $C_6H_5.PCl_4$, which melts at 73° ; with *bromine* to form $C_6H_5.PCl_2Br_2$, melting at 208° ; with oxygen to form the oxychloride, $C_6H_5.PCl_2O$, which is a liquid boiling, with partial decomposition, at 260° ; and with *sulphur* to form $C_6H_5.PCl_2S$, a liquid boiling, also with partial decomposition, at 270°.

Phosphenylous Acid, $C_6H_5.PHO.OH$, formed, as above mentioned, by the action of water on the dichloride, crystallises in colourless laminæ, melting at 70°, and acts as a powerful reducing agent. Phosphenylic acid, $C_6H_5.PO(OH)_2$, formed in like manner from the tetrachloride, crystallises in laminæ, melting at 158°.

Phenyl-phosphine, $C_6H_5.PH_2$.—Dry hydriodic acid gas passed into phosphenyl chloride unites with it forming the compound, $C_6H_5.PI_2.HI$, which is decomposed by alcohol, with formation of phenylphosphine. The latter is a liquid having a pungent and offensive odour, heavier than water, boiling at 160°. It oxidises in the air, forming phosphenyl oxide, $C_6H_5.PH_2O$, a crystalline mass easily soluble in water. Phenyl-phosphine does not dissolve in aqueous acids, but unites with dry *hydrogen iodide*, forming phenylphosphonium iodide, $C_6H_5.PH_3I$, from which the phenylphosphine may be separated by water.

Diethyl-phenylphosphine, $C_6H_5.P(C_2H_5)_2$, formed by the action of zinc-ethyl on phosphenyl chloride, and treatment of the product with caustic soda, is a colourless strong-smelling liquid, having a specific gravity of 0·9571 at 13°, boiling at 222°, insoluble in water, soluble in acid, but not forming crystallisable salts. With ethyl iodide it forms the compound $C_6H_5.P(C_2H_5)_3I$, which is crystalline, and easily soluble in water.

Arsenic Compounds.—*Arseniophenyl chloride*, $C_6H_5AsCl_2$, formed by the action of arsenious chloride on mercury-diphenyl, is a heavy colourless liquid, boiling at 252°–255°, not decomposed by water, soluble in alkalis. It unites with chlorine, forming a reddish-yellow liquid *tetrachloride*, $C_6H_5AsCl_4$, which is decomposed by water into hydrochloric and phenylarsinic acids, $C_6H_5AsO(OH)_2$, crystallising in long needles which melt at 168°.

Arsenio-diphenyl chloride, or *Phenylcacodyl chloride*, $(C_6H_5)_2AsCl$, formed in small quantity, together with the preceding compound, is a thick oil, boiling above 360°, not decomposed by water. It unites with *chlorine*, forming the trichloride, $(C_6H_5)_2AsCl_3$, which melts at 174°, and is decomposed by warm water into hydrochloric acid and phenylcacodylic acid, $(C_6H_5)_2AsO.OH$, which crystallises in needles, slightly soluble in water, melting at 174°.

Silico-phenyl Compounds.—The *chloride*, $C_6H_5SiCl_3$, obtained by heating mercury-diphenyl with silicic chloride, $SiCl_4$, to 300°, is a liquid which fumes in the air, and boils at 197°. It is decomposed by water, with formation of silico-benzoic acid, $C_6H_5.SiO.OH$, *i.e.*, benzoic acid in which the C of the group COOH is replaced by Si. With alcohol, the triethylic ether, $C_6H_5.Si(OC_2H_5)_3$, is formed, as a liquid boiling at 237°.

Mercury-diphenyl, $(C_6H_5)_2Hg$, is formed by heating a solution of bromobenzene in benzene for a considerable time with liquid sodium-amalgam, the reaction being facilitated by addition of a little acetic ether. It crystallises in colourless rhombic prisms, melts at 120°, and may be sublimed; turns yellow on exposure to the air; dissolves easily in benzene and carbon sulphide; less easily in ether and in alcohol; not at all in water. When distilled it is for the most part decomposed into diphenyl, benzene, and mercury. Acids decompose it, with formation of benzene and mercury salts. When treated with two molecules of chlorine, bromine, or iodine, it is decomposed into monochloro-benzene, &c., and a halogen-compound of mercury; *e.g.*,

$$(C_6H_5)_2Hg + 2Cl_2 = 2C_6H_5Cl + HgCl_2.$$

With one molecule of the halogen element, haloid-compounds are formed, like $C_6H_5.HgI$, from which, by the action of moist silver oxide, the hydroxide, $C_6H_5.Hg.OH$, is formed, a crystalline, strongly alkaline compound, which expels ammonia from ammonium salts.

Amido-toluenes.

These, like other toluene derivatives, admit of metameric modifications, according as the NH_2-group is situated in the principal or the lateral chain (p. 424).

Toluidine, $C_7H_9N = C_6H_4(NH_2).CH_3$.—This base, homologous with aniline, exhibits the three modifications, ortho-, meta-, and para-, which are obtained by reduction of the three corresponding nitrotoluenes, $C_6H_4(NO_2).CH_3$.

Para-toluidine (ordinary toluidine), $C_6.CH_3.H.H.NH_2.H_2$, forms large colourless tabular crystals, heavier than water, very sparingly soluble in water, easily in alcohol and ether. It melts at 45°, boils at 198°; has an aromatic taste and odour, a very feeble alkaline reaction; does not give any coloured reaction with chloride of lime. It forms crystalline salts, but is a weak base, incapable of neutralising sulphuric acid. With acetyl chloride it forms acetoparatoluidine, $C_6H_4(NH.C_2H_3O).CH_3$, a crystalline compound melting at 145°.

Ortho-toluidine, also called *Pseudo-toluidine*, is a colourless, neutral liquid, becoming rose-coloured on exposure to the air. It has a density of 1·00 at 16°, boils at 199·5°, and does not solidify at −20°. Its acetyl-derivative melts at 107°.

Meta-toluidine, from metanitrotoluene, is a colourless liquid, of specific gravity 0·998 at 15°, boiling at 197°, not solidifying at −13°. Its acetyl-derivative melts at 65·5°.

Commercial toluidine, from aniline works, is a mixture of ortho- and para-toluidine, the latter of which partly crystallises out on cooling to a low temperature. To separate the ortho-toluidine from the still dissolved para-modification, the liquid is heated with glacial acetic acid, whereby the two bases are converted into acetotoluides; these are dissolved in strong acetic acid, and the solution is diluted with 80 parts of water, whereby the acetoparatoluide is precipitated, while the acetorthotoluide remains in solution; or the mixture of the two bases is heated successively with oxalic acid and ether, whereby an oxalate of paratoluidine is first separated, the ortho-salt remaining dissolved.

Benzylamine, $C_6H_5.CH_2(NH_2)$ or $NH_2(C_7H_7)$.—This compound, metameric with toluidine, is obtained, together with *dibenzylamine*, $NH(C_7H_7)_2$, and *tribenzylamine*, $N(C_7H_7)_3$, by the action of alcoholic ammonia on benzyl chloride, $C_6H_5.CH_2Cl$ (p. 439).

Benzylamine is a colourless liquid, boiling at 185°. It mixes in all proportions with water, and is separated therefrom by potash. It is much stronger base than toluidine; absorbs carbon dioxide rapidly, forming a crystalline carbonate; unites readily with acids, producing rise of temperature; and fumes with hydrochloric acid. The hydrochloride crystallises in striated tables; the platinochloride, $2NH_3(C_7H_7)Cl.PtCl_4$, in orange-coloured laminæ.

Dibenzylamine, $(C_7H_7)_2NH$, is a colourless viscid liquid, insoluble in water, easily soluble in alcohol and ether; having a specific gravity of 1·033 at 14°.

Tribenzylamine, $(C_7H_7)_3N$, forms colourless needles or laminæ, melting at 91°, insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol and in ether. Its hydrochloride, heated in a stream of dry hydrogen chloride, is resolved into benzyl chloride and the hydrochloride of dibenzylamine.

Diamidotoluenes or **Tolylene-diamines**, $C_6H_3(NH_2)_2.CH_3$.—The modification 1 : 2 : 4 (CH_3 in 1), obtained by reduction of dinitrotoluene melting at 70·5°, with tin and hydrochloric acid, crystallises in long needles, melts at 99°, and boils at 280°. 1 : 3 : 4, obtained by reduction of metanitro-paratoluidine, forms colourless scales, melting at 88·5°, boiling at 265°.

Metaxylidine, $C_8H_{11}N = C_6H_3(NH_2).(CH_3)_2$, **Cumidine**, $C_9H_{13}N$, or probably $C_6H_4(NH_2).C_3H_7$, and **Cymidine**, $C_{10}H_{15}N$, or $C_{10}H_{13}(NH_2)$, homologous with toluidine, are obtained in like manner by reduction of the corresponding nitro-derivatives. Xylidine boils at 214°–216°; cumidine at 225°; cymidine at 250°. Xylidine and cumidine form well-crystallised salts.

Mesidine or Amidomesitylene, $C_6H_2(CH_3)_3.NH_2$ (the three CH_3-groups symmetrical, 1 : 3 : 5) is liquid. *Nitromesidine*, $C_9H_{10}(NO_2)(NH_2)$, melts at 100°; *diamidomesitylene*, $C_9H_{10}(NH_2)_2$, at 90°.

Xylylamine, $C_8H_{11}N = NH_2C_8H_9 = C_6H_4(CH_3).CH_2NH_2$, homologous with benzylamine, is obtained, together with *dixylylamine*, $NH(C_8H_9)_2$, and *trixylylamine*, $N(C_8H_9)_3$, by heating xylyl chloride, $C_6H_4(CH_3).CH_2.Cl$, with alcoholic ammonia in sealed tubes. These three bases are oily liquids, smelling like herring-pickle, lighter than water, insoluble therein, easily soluble in alcohol and ether. Xylylamine boils at 196°; dixylylamine decomposes at 210°.

Cumylamine, the 9-carbon base metameric with cumidine and homologous with benzylamine, has not been obtained.

Cymylamine, $C_{10}H_{15}N = NH_2(C_{10}H_{13}) = C_6H_4(CH_3).C_3H_6(NH_2)$, is obtained, together with *di-* and *tri-cymylamine*, by heating cymyl chloride with alcoholic ammonia in sealed tubes. Cymylamine and dicymylamine are oily liquids, boiling with decomposition, the former at 280°, the latter above 300°. *Tricymylamine* crystallises in rhomboïdal laminæ, melting at 81°–82°.

ANILINE DYES.

Aniline has during the last few years found an extensive application in the arts, a long series of colouring matters unequalled in brilliancy and beauty, having, by the action of different oxidising agents, been produced from it. It was Mr W. H. Perkin who first conceived the happy idea of applying practically the well-known property possessed by aniline, of forming violet and blue solutions when treated with a solution of chloride of lime or chromic acid. He succeeded in fixing these colours, and bringing them into a form adapted for the dyer.

Aniline-purple or **Mauve**, the first discovered of the aniline-dyes (1856), is prepared by mixing solutions of aniline sulphate and potassium bichromate in equivalent proportions, and allowing the mixture to stand for several hours. The black precipitate formed is filtered off and purified from admixed potassium sulphate by washing with water; it is then dried and freed from resinous matter by repeated digestion with coal-tar naphtha, and finally dissolved in boiling alcohol. For its further purification, the alcoholic solution is evaporated to dryness, the substance is dissolved in a large quantity of boiling water, reprecipitated with caustic soda, washed with water, and dissolved in alcohol; and the filtered solution is evaporated to dryness. Mauve thus prepared forms a brittle substance, having a beautiful bronze-coloured surface: it is difficultly soluble in cold water, although it imparts a deep purple colour to that liquid: it is more soluble in hot water, very soluble in alcohol, nearly insoluble in ether and hydrocarbons: it dissolves in concentrated acetic acid, from which it crystallises. Mauve is the sulphate of a base called mauveïne, having the composition $C_{26}H_{24}N_4$, and capable of forming crystalline salts with acids.

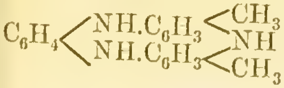
Aniline-red, Rosaniline, $C_{20}H_{19}N_3$ (or $C_{20}H_{17}N_3$).—Salts of this base occur more or less pure in commerce under the names *roseine, fuchsine, magenta, azaleine,* &c. A red colour had been observed at different times in experimenting with aniline, more especially when that substance was digested with Dutch liquid. The red colouring matter, though still impure, was first obtained in a separate state from the product formed by digesting aniline with carbon tetrachloride at 150°, in which reaction it is formed, together with triphenylguanidine. Verguin (1858) first prepared it on a large scale by the action of stannic chloride upon aniline; and it has since been produced by the action of mercuric salts, arsenic acid, and many other oxidising agents, upon aniline. The most advantageous mode of preparation is the following:—A mixture of 12 parts of the dry arsenic acid which occurs in commerce, and 10 parts of aniline, is heated to 120° or 140° C. (250°–280° F.), with addition of water, for about six hours. The product, which is a hard mass having the lustre of bronze, is dissolved in hot water and precipitated by a slight excess of soda; the precipitate when washed with water, and dissolved in acetic acid, forms the roseine of commerce. In order to purify this still crude substance, it is boiled with an excess of soda, to separate any aniline that it may contain; and the washed precipitate is dissolved in very dilute mineral acid, filtered from undissolved tarry matter, and reprecipitated with alkali. The compounds of rosaniline with one molecule of acid are beautifully crystallised substances, which in the dry state have a green colour with golden lustre; with water they yield a very intensely coloured red solution. The free base, first obtained by Nicholson, presents itself in colourless crystalline plates, insoluble in water, soluble in alcohol and ether, with a red colour, which it also acquires on exposure to the air.

Rosaniline in the anhydrous state is represented by the formula, $C_{20}H_{19}N_3$, and in the hydrated state, such as it assumes when isolated from its compounds, by the formula $C_{20}H_{19}N_3.H_2O$. It is a triamine capable of forming monoacid, biacid, and triacid salts. The aniline-reds of commerce are monoacid salts of rosaniline more or less pure. The acetate, which is chiefly found in commerce in England, has been prepared by Nicholson in splendid crystals of very considerable dimensions, having the composition $C_{20}H_{19}N_3.C_2H_4O_2$. In France the hydrochloride, $C_{20}H_{19}N_3.HCl$, is chiefly employed. The action of ammonium sulphide upon rosaniline gives rise to *leucaniline*, $C_{20}H_{21}N_3$, a base containing two additional atoms of hydrogen. This base is itself colourless, and forms colourless triacid salts, such as $C_{20}H_{21}N_3.3HCl$. Oxidising agents reconvert it into rosaniline.

The molecular constitution of rosaniline has not been distinctly made out, and there is even some doubt (as above indicated) with respect to its empirical formula. Its mode of formation, also, is not thoroughly understood; but one very important fact has been brought to light by the researches of Hofmann, and confirmed by the experience of manufacturers,—namely, that pure aniline, from whatever source it may be obtained, is incapable of furnishing aniline-red. Commercial aniline prepared from coal-tar always in fact contains toluidine as well as aniline; and Hofmann has shown that the presence of this base, together with aniline, is essential to the formation of the red dye. Toluidine by itself is just as incapable of yielding the red as pure aniline, but when a mixture of pure aniline and pure toluidine is treated with stannic or mercuric chloride, or with arsenic acid, the red colouring matter is immediately produced. If the formula $C_{20}H_{19}N_3$ be correct, the formation of rosaniline may perhaps be represented by the equation:

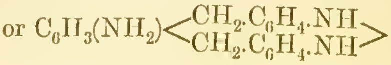
$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3H_2\,;$$

and its structure by the formula:



$$C_6H_4\left\langle\begin{matrix}NH.C_6H_3\left\langle\begin{matrix}CH_3\\NH\end{matrix}\right.\\NH.C_6H_3\left\langle\begin{matrix}\\CH_3\end{matrix}\right.\end{matrix}\right.$$

or



$$C_6H_3(NH_2)\left\langle\begin{matrix}CH_2.C_6H_4.NH\\CH_2.C_6H_4.NH\end{matrix}\right\rangle$$

But rosaniline is converted by nitrous acid into aurin or rosolic acid, which, according to the recent experiments of Dale and Schorlemmer,* has the composition $C_{20}H_{14}O_3$, and is reconverted into rosaniline by heating with alcoholic ammonia. According to this, rosaniline should have the formula $C_{20}H_{17}N_3$, the two reactions just mentioned being represented by the equations:

$$C_{20}H_{17}N_3 + 3NO_2H = C_{20}H_{14}O_3 + 3H_2O + 3N_2,$$

and

$$C_{20}H_{14}O_3 + 3NH_3 = C_{20}H_{17}N_3 + 3H_2O.$$

Aniline-blue and **Aniline-violet.**—Girard and De Laire obtained aniline-blue by digesting rosaniline with an excess of aniline at 150°–160° C. (300°–320° F.). Together with aniline-blue, which is the principal product of the reaction, several other colouring matters (violet and green), and indifferent substances, are formed, considerable quantities of ammonia being invariably evolved. The crude blue is purified by treating it successively with boiling water acidified with hydrochloric acid, and with pure water. The blue colouring matter is said to be obtained from its boiling alcoholic solution in brilliant needles. It consists of the hydrochloride of *triphenyl-rosaniline*, $C_{20}H_{16}(C_6H_5)_3$. By heating rosaniline with ethyl iodide, Hofmann has obtained an aniline-violet, having the composition of hydriodide of *triethyl-rosaniline*, $C_{20}H_{16}(C_2H_5)_3N_3$. Another aniline-violet is produced by heating rosaniline with a quantity of aniline less than sufficient to form aniline-blue.

Other aniline violets are produced by the action of stannic chloride, mercuric chloride, or iodine chloride on methyl-aniline and dimethyl-aniline.

Aniline Greens.—The most important of these colours are those known as "aldehyde-green" and "iodine green." The former is produced by adding $1\frac{1}{2}$ parts aldehyde to a cold solution of magenta in a mixture of 3 parts strong sulphuric acid and 1 part water. The mixture is then heated in a water-bath till a drop of the product diffused in water produces a fine blue colour, and then poured into a boiling solution of sodium thiosulphate. The liquid is then boiled for a short time and filtered. The filtrate contains the green, which may be precipitated by tannin or by sodium-acetate. Aldehyde-green is principally used in silk-dyeing. It is a salt of an organic base which may be separated by means of soda or ammonia.

Iodine-green is produced by heating the violets of triethyl- or trimethyl-rosaniline (Hofmann's violets) or the methyl-aniline violets, with iodide of methyl, ethyl, or amyl. The green thus obtained with methyl iodide has a very fine colour, bluer than that of aldehyde-green, and, like the latter, preserves its colour by artificial light. It is much used for cotton and silk dyeing.

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* Chem. Soc. Journal, 1877, vol. ii. p. 121.

A third kind of aniline-green, known commercially as "Perkin's green," resembles the iodine-green, and is much used for calico-printing.

Chrysaniline, $C_{20}H_{17}N_3$ (or $C_{20}H_{15}N_3$?), is formed as a secondary product in the preparation of aniline-red. It is a well-defined base, forming two series of salts, most of which are well crystallised. The two hydrochlorides of chrysaniline are $C_{20}H_{17}N_3.HCl$, and $C_{20}H_{17}N_3.2HCl$. The nitrate, $C_{20}H_{17}N_3.NO_3H$, is so little soluble in water, that nitric acid may be precipitated even from a dilute solution of nitrates by means of the more soluble hydrochloride or acetate of chrysaniline.

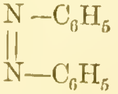
Aniline-Brown is obtained by heating 4 parts of aniline hydrochloride to 240° with 1 part of aniline-violet or aniline-blue.

Aniline-Black.—Blacks of great intensity are produced on calico by printing with a mixture of aniline, potassium chlorate, and a metallic compound,—the one most generally used being cupric sulphide. The composition of aniline-black is not known, neither is its mode of formation well understood; but it appears to depend upon oxidation of the aniline by the chlorate and the cupric sulphide, these compounds being thereby reduced, and afterwards reoxidised by the oxygen of the air, so that they act as carriers of oxygen. The finest black is obtained with vanadium salts, which easily undergo oxidation and reduction.

Aniline also forms colouring matters with xylidine. *Xylidine-rosaniline*, produced according to the equation $C_6H_7N + 2C_8H_{11}N = C_{22}H_{33}N_3 + 3H_2$, forms salts of a fine crimson colour.

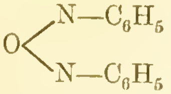
AZO- AND DIAZO-COMPOUNDS.

These compounds are derived from the aromatic hyrocarbons by substitution of 2 atoms of nitrogen for 2 atoms of hydrogen, the nitrogen apparently acting as a univalent radicle. In the azo-compounds the two nitrogen-atoms are united to one another by a part of their combining capacities, and each is directly combined with the carbon of a benzene-residue; thus:

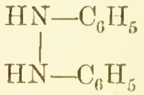


$$\begin{matrix} N-C_6H_5 \\ \| \\ N-C_6H_5 \end{matrix}$$

Azobenzene.



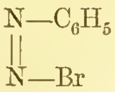
Azoxybenzene.



$$\begin{matrix} HN-C_6H_5 \\ | \\ HN-C_6H_5 \end{matrix}$$

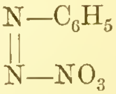
Hydrazobenzene.

In the diazo-compounds, only one of the nitrogen-atoms is directly linked to the carbon of a benzene-residue, while the free combining unit of the other is satisfied either by a halogen-element or by an acid residue, or generally in some way different from the first; thus:



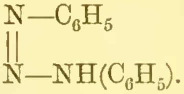
$$\begin{matrix} N—C_6H_5 \\ \| \\ N—Br \end{matrix}$$

Diazobenzene Bromide.



$$\begin{matrix} N—C_6H_5 \\ \| \\ N—NO_3 \end{matrix}$$

Diazobenzene Nitrate.



$$\begin{matrix} N—C_6H_5 \\ \| \\ N—NH(C_6H_5). \end{matrix}$$

Diazobenzene-amidobenzene.

The azo-compounds are formed: 1. By the action of certain reducing agents on the nitro-derivatives of the aromatic hydrocarbons; 2. By oxidation of aniline. They may indeed be regarded as stepping-stones from the nitro- to the amido-derivatives, as shown by the following formulæ:

	Equivalent formulæ.	Molecular formulæ.
Nitrobenzene,	$C_6H_5NO_2$	$C_6H_5NO_2$
Azoxybenzene,	$C_6H_5NO_{\frac{1}{2}}$	$C_{12}H_{10}N_2O$
Azobenzene,	C_6H_5N	$C_{12}H_{10}N_2$
Hydrazobenzene,	C_6H_6N	$C_{12}H_{12}N_2$
Amidobenzene,	C_6H_7N	C_6H_7N.

The hydrogen of the benzene-nucleus in these bodies may be partly replaced by the halogen-elements and the groups NO_2, NH_2, SO_3H, &c.

Azoxybenzene, $C_{12}H_{10}N_2O$, or *Azoxybenzide*, is formed by the action of potash or soda, or of sodium-amalgam on nitrobenzene in alcoholic solution. Nitrobenzene (1 vol.) is dissolved in strong alcohol (8–10 vol.) and a quantity of dry potassium hydroxide, equal in weight to the nitrobenzene, is added; the liquid, which becomes heated spontaneously, is boiled for some time; the alcohol is then distilled off till the residual liquid separates into two layers; and the upper brown layer, which contains the azoxybenzene, is washed with water, whereupon it solidifies to a crystalline mass, which is recrystallised from alcohol.

Azoxybenzene forms long yellow needles, insoluble in water, easily soluble in alcohol and ether. It melts at 36°, and is decomposed by distillation into aniline and azobenzene. By reducing agents it is converted into azobenzene and hydrazobenzene. It yields two mononitro-derivatives, one melting at 143°, the other at 49°.

Azobenzene, $C_{12}H_{10}N_2$, *Azobenzide*, is formed by the action of iron and acetic acid, or better of sodium-amalgam, on nitrobenzene. On heating the products, the azobenzene distils over as a yellow oil, which solidifies in the receiver, while azoxybenzene remains behind.

Azobenzene crystallises in large yellowish-red laminæ, sparingly soluble in water, easily in alcohol and ether. It melts at 66·5, and distils at 293°. By the action of ammonium sulphide and other reducing agents it is converted into hydrazobenzene and the isomeric compound benzidine. With bromine it forms the compound $C_{12}H_{10}Br_2N_2$ or $C_6H_5—BrN—NBr—C_6H_5$, and with nitric acid a mono- and a dinitro-derivative.

Amidazobenzene or Amidodiphenylimide, $C_{12}H_9(NH_2)N_2 = C_6H_5—N{=}N—C_6H_4(NH_2)$.—This compound, which forms the chief constituent of commercial aniline-yellow, is produced by the action of ammonium sulphide on nitro-azobenzene, and by a molecular transformation of the isomeric compound diazo-amidobenzene, $C_6H_5—N{=}N—NH(C_6H_5)$, which takes place when the latter is left in contact with alcohol and aniline hydrochloride; also by the action of sodium stannate and other oxidising agents on aniline.

Amidazobenzene crystallises from hot alcohol in yellow rhombic needles or prisms, sparingly soluble in hot water, melting at 127·4°, and sublimable. It forms crystalline salts containing 1 equivalent of acid, yellow or violet in the solid state, decomposed by water. By distillation with sulphuric acid and manganese dioxide, it is oxidised to quinone, $C_6H_4O_2$. By the action of tin and hydrochloric acid, it is resolved into aniline and diamidobenzene.

Diamid-azobenzene or Diphenine, $C_{12}H_8(NH_2)_2N_2$, formed by reduction of dinitro-azobenzene with ammonium sulphide, is a yellow crystalline base, dissolving with red colour in acids, resolved by reducing agents into two molecules of diamidobenzene:

$$C_{12}H_8(NH_2)_2N_2 + 2H_2 = 2C_6H_4(NH_2)_2 .$$

Hydrazobenzene, $C_{12}H_{12}N_2$, formed by the action of ammonium sulphide or sodium-amalgam on azobenzene or azoxybenzene, crystallises in large plates, having a peculiar camphorous odour. It dissolves easily in alcohol and ether, but is insoluble in water; melts at 131°. In contact with dilute mineral acids, it is easily converted into the isomeric compound, benzidine or diamidodiphenyl, $NH_2.C_6H_4—C_6H_4.NH_2$ (see DIPHENYL COMPOUNDS). By the action of oxidising agents, or by contact of its alcoholic solution with the air, it is converted into azobenzene. By distillation it is resolved into aniline and azobenzene.

Diamidhydrazobenzene, $C_{12}H_{10}(NH_2)_2N_2$, produced by the action of sodium-amalgam on metanitraniline, forms yellow needles melting at 140°.

Azotoluene, $C_{14}H_{14}N_2$, formed by treating an alcoholic solution of nitrotoluene with sodium-amalgam, with occasional addition of acetic acid, crystallises in orange-red shining needles, which melt at 137°, and sublime without decomposition. It is insoluble in water, dilute acids, and alkalis, but dissolves easily in alcohol and ether. Treated in alcoholic solution with sodium-amalgam or ammonium sulphide, it is converted into hydrazotoluene, $C_{14}H_{16}N_2$. With bromine it yields a crystalline addition-product, $C_{14}H_{14}Br_2N_2$.

Diazo-compounds.

These compounds, the structure of which has been already explained, are formed by the action of nitrous acid on the salts of the amido-derivatives of the aromatic hydrocarbons; thus:

$$C_6H_5NH_2.NO_3H \quad + \quad NO.OH \quad = \quad C_6H_5.N_2.NO_3 \quad + \quad 2H_2O.$$

Aniline nitrate. Diazobenzene nitrate.

They are, however, somewhat unstable, and are apt to be decomposed by the water resulting from the reaction, especially if the liquid is hot, with evolution of nitrogen, and formation of hydroxyl-derivatives, *i.e.*, phenols:

$$C_6H_5.N_2.NO_3 \quad + \quad H_2O \quad = \quad C_6H_5.OH \quad + \quad N_2 \quad + \quad NO_3H,$$

Diazobenzene nitrate. Phenol.

the final result being the same as if the nitrous acid acted on the aromatic amido-compound in the same way that it acts upon the amines and amides of the fatty series (p. 215):

$$C_6H_5.NH_2 + NO.OH = C_6H_5.OH + H_2O + N_2.$$

A better mode of preparing the diazo-compound is to add solution of potassium nitrite to a solution of the amido-compound in nitric acid:

$$C_6H_5(NH_2).NO_3H + NO_2K + NO_3H = C_6H_5.N_2.NO_3 + NO_3K + 2H_2O.$$

Amido-compounds in which the hydrogen of the NH_2-group is partly or wholly replaced by alcohol-radicles, generally yield the same diazo-compounds as the original amido-derivatives, the alcohol-radicles being separated in the form of alcohols:

$$C_6H_5.NH(C_2H_5).NO_3H + NO_2H = C_6H_5.N_2.NO_3 + C_2H_5OH + H_2O$$

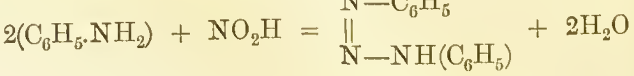
Ethyl-aniline nitrate. Diazo-benzene nitrate.

$$C_6H_5.N(C_2H_5)_2.NO_3H \quad + \quad NO_2H \quad = \quad C_6H_5.N_2.NO_3 \quad + \quad 2C_2H_5OH.$$

Diethyl-aniline nitrate.

Those, on the contrary, in which the hydrogen of the benzene-nucleus is partly replaced by Cl, Br, NO_2, &c., yield substituted diazo-compounds, such as $C_6H_4Cl.N_2.NO_3$, $C_6H_4(NO_2).N_2.NO_3$, &c.

When nitrous acid acts upon an amido-compound in the free state in alcoholic or ethereal solution, the product is a diazo-amido-compound; thus:



$$2(C_6H_5.NH_2) + NO_2H = \begin{array}{l} N-C_6H_5 \\ \| \\ N-NH(C_6H_5) \end{array} + 2H_2O$$

Aniline. Diazo-amidobenzene.

These compounds are also formed by the action of amines or their salts on the salts of diazo-compounds:

$$C_6H_5.N_2.NO_3 + 2(C_6H_5.NH_2) = C_6H_5.N_2.NH(C_6H_5) + C_6H_7N.NO_3H$$

$$C_6H_5.N_2.OK + C_6H_5.(NH_2).HCl = C_6H_5.N_2.NH(C_6H_5) + KCl + H_2O.$$

By this reaction, also, mixed diazo-amido-compounds may be obtained; for example, diazotoluene-amidobenzene, $C_7H_7.N_2.NH.C_6H_5$, from toluidine and a salt of diazobenzene.

In like manner, diazo-amido-compounds may be formed with the primary and secondary amines of the fatty series: *e.g.*,

$$\underset{\text{Diazobenzene nitrate.}}{C_6H_5.N_2.NO_3} + \underset{\text{Diethylamine.}}{2(C_2H_5)_2NH} = \underset{\text{Diazobenzene-diethylamine.}}{C_6H_5.N_2.N(C_2H_5)_2} + \underset{\text{Diethylamine nitrate.}}{(C_2H_5)_2NH.NO_3H}$$

The diazo-compounds are mostly colourless crystalline bodies, which quickly turn brown on exposure to the air. They dissolve easily in water, sparingly in alcohol, and are precipitated from the alcoholic solutions by ether. Most of them are very unstable, and decompose with explosion when heated or struck. They suffer decomposition also under the influence of the most various reagents, generally in such a manner that both the nitrogen-atoms are eliminated in the gaseous form, and the diazo-group is replaced by halogen elements, hydrogen, hydroxyl, &c.

1. When boiled with *water*, they yield phenols:

$$C_6H_5.N_2.Br + H_2O = C_6H_5.OH + N_2 + HBr.$$

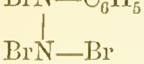
With *hydrogen sulphide* in like manner they yield mercaptans.

2. On boiling them with strong *alcohol*, the N_2-group is replaced by hydrogen, producing benzene or a homologous hydrocarbon, while the alcohol is oxidised to aldehyde:

$$C_6H_5.N_2.NO_3 + C_2H_5OH = C_6H_6 + N_2 + NO_3H + C_2H_4O.$$

3. The *platinochlorides*, formed by combination of the diazo-chlorides with $PtCl_4$, are decomposed when heated alone, or better with dry sodium carbonate and common salt, producing chlorinated hydrocarbons, which distil over:

$$(C_6H_5.N_2.Cl)_2.PtCl_4 = 2C_6H_5Cl + 2N_2 + 2Cl_2 + Pt.$$

4. The *diazobromides* take up two atoms of bromine, forming perbromides, such as $C_6H_5N_2Br_3$, or 
$\begin{matrix} BrN—C_6H_5 \\ | \\ BrN—Br \end{matrix}$, which are likewise decomposed by dry distillation, or more readily by boiling with strong alcohol, yielding monobromo-derivatives of the hydrocarbons:

$$C_6H_5.N_2.Br_3 = C_6H_5Br + Br_2 + N_2.$$

5. The sulphates and other oxy-salts of the diazo-compounds, boiled with *hydriodic acid*, yield iodine-derivatives:

$$C_6H_5.N_2.SO_4H + HI = C_6H_5I + N_2 + SO_4H_2.$$

Diazo-compounds containing chlorous radicles (Cl, Br, NO_2, &c.) in the benzene-nucleus undergo exactly similar decompositions; *e.g.*,

$$\underset{\text{Diazo-bromobenzene nitrate.}}{C_6H_4Br.N_2.NO_3} + H_2O = \underset{\text{Bromophenol.}}{C_6H_4.Br.OH} + N_2 + NO_3H$$

$$\underset{\text{Diazo-dichlorobenzene perbromide.}}{C_6H_3Cl_2.N_2.Br_3} = \underset{\text{Bromodichlorobenzene.}}{C_6H_3Cl_2Br} + Br_2 + N_2.$$

The reactions 1, 3, 4, and 5 afford the means of converting an aromatic amido-derivative (and therefore also a nitro-derivative), through the medium of the diazo-compound, into the corresponding halogen- and hydroxyl-derivatives; and this mode of transformation, known as the "diazo-reaction" serves, as already shown in several instances, to determine the relative positions of the substituted radicles in these derivatives (p. 436).

The diazo-amido-compounds, which may be regarded as formed by the union of diazo- and amido-derivatives, undergo similar transformations. They are first resolved, under the influence of hydrobromic or hydrochloric acid, &c., into their components, a diazo- and an amido-derivative; the latter then separates out either in the free state, or as a salt, and the diazo-compound is transformed in the manner above described; thus:

$$C_6H_5.N_2NH(C_6H_5) + 2HBr = C_6H_5Br + N_2 + C_6H_5(NH_2).HBr$$

$$C_6H_5.N_2.NH(C_6H_5) + H_2O = C_6H_5OH + N_2 + C_6H_5.NH_2.$$

Diazobenzene-compounds.—The *nitrate*, $C_6H_5.N_2.NO_3$, is prepared by passing nitrous acid vapour into a flask containing aniline nitrate moistened with a small quantity of water and cooled with ice, till the whole is dissolved, and the solution no longer yields aniline when mixed with potash. On filtering the liquid, and adding alcohol and ether, the diazobenzene nitrate separates as a crystalline mass, which may be purified by redissolution in a small quantity of cold water, and precipitation by alcohol and ether.

Diazobenzene nitrate forms long colourless needles, extremely soluble in water, slightly soluble in alcohol, insoluble in ether and in benzene. It is tolerably permanent when dry, but gradually turns brown on exposure to moist air. It explodes violently when heated.

The *sulphate*, $C_6H_5.N_2.SO_4H$, is prepared by passing nitrous acid into aniline sulphate dissolved in water containing sulphuric acid, or better, by decomposing the nitrate with sulphuric acid. It forms colourless needles or prisms easily soluble in water, exploding at 100°.

The *bromide*, $C_6H_5.N_2.Br$, separates in white laminæ on gradually adding bromine dissolved in ether to an ethereal solution of diazo-amidobenzene, while tribromaniline, which is formed at the same time, remains in solution.

The *perbromide*, $C_6H_5.N_2.Br_3$, is formed by mixing an aqueous solution of the nitrate with a solution of bromine in hydrobromic acid or sodium bromide, and separates as a dark-brown oil, which soon solidifies to a crystalline mass. When recrystallised by solution in cold alcohol, and rapid evaporation in a vacuum, it may be obtained in large yellow laminæ, insoluble in water and ether, moderately soluble in cold alcohol. By prolonged washing with ether, it is converted into the monobromide.

The *chloride*, $C_6H_5.N_2Cl$, is obtained in solution by agitating a solution of the bromide with moist silver chloride.

The *platinochloride*, $(C_6H_5N_2Cl)_2PtCl_4$, is precipitated in yellow prisms on adding a solution of platinic chloride to a solution of the nitrate or sulphate.

Diazobenzene-potassium, $C_6H_5.N_2.OK$, separates on adding caustic potash to a solution of the nitrate, as a yellow liquid, which, when evaporated over the water-bath, crystallises in white nacreous laminæ, easily soluble in water and in alcohol. The aqueous solution quickly decomposes, and when mixed with silver nitrate, yields a grey precipitate of $C_6H_5N_2.OAg$, and similar precipitates with mercury, lead, zinc, and other metals. On adding acetic acid to a solution of the potassium compound, a heavy oil is precipitated, probably consisting of diazobenzene hydroxide, $C_6H_5.N_2.OH$.

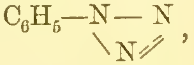
Diazo-amidobenzene, $C_6H_5.N_2.NH.C_6H_5$, is formed by the action of nitrous acid on aniline dissolved in alcohol; also by mixing a solution of diazobenzene nitrate with aniline; and by gradually pouring a cooled, slightly alkaline solution of sodium nitrite on aniline hydrochloride. It crystallises in golden-yellow shining laminæ, melts at 91°, and detonates at a higher temperature. It is insoluble in water, easily soluble in ether, benzene, and hot alcohol. By nitric acid containing nitrous acid, it is converted into diazobenzene nitrate; by strong hydrochloric acid into aniline hydrochloride, phenol, and nitrogen.—The alcoholic solution mixed with silver nitrate deposits the compound $C_6H_5.N_2.NAg.C_6H_5$, in reddish needles.

Diazo-amidobenzene does not unite with acids, but its alcoholic solution mixed with a solution of platinic chloride in hydrochloric acid, yields the platinochloride $(C_{12}H_{11}N_3.HCl)_2.PtCl_4$, in reddish needles.

Diazo-amidobenzene in alcoholic solution, especially if in contact with a small quantity of aniline hydrochloride, gradually changes into the isomeric compound amidazobenzene, $C_6H_5.N{=}N.C_6H_4.NH_2$ (p. 467).

Diazobenzene-dimethylamide, $C_6H_5.N_2.N(CH_3)_2$, formed by mixing the aqueous solutions of diazobenzene nitrate and dimethylamine, is a yellow, oily liquid, having weak basic properties, and forming unstable salts, which in aqueous solution are easily resolved into phenol, nitrogen, and salts of dimethylamine.

Diazobenzene-ethylamide, $C_6H_5.N_2.NH(C_2H_5)$, resembles the dimethyl-compound, and is formed in a similar manner.

Diazobenzenimide, $C_6H_5N_3$, probably  $\begin{array}{l}C_6H_5-N-N\\ \qquad\quad\diagdown N \diagup\!\!\diagup\end{array}$, is formed by the action of aqueous ammonia on diazobenzene perbromide:

$$C_6H_5N_2Br_3 + 4NH_3 = 3NH_4Br + C_6H_5N_3.$$

It is a yellow oil, insoluble in water, distilling without decomposition in rarefied air and in vapour of water, dissolving without alteration in nitric and sulphuric acid. Treated in alcoholic solution with zinc and hydrochloric acid, it is resolved into ammonia and aniline:

$$C_6H_5N_3 + 4H_2 = 2NH_3 + C_6H_5.NH_2.$$

The diazo-compounds of higher orders, *e.g., diazotoluene nitrate,* $C_7H_7.N_2.NO_3$, *diazo-amidotoluene,* $C_7H_7.N_2.NH.C_7H_7$, &c., are analogous to the diazo-benzene compounds; but they have not been much examined.

HYDRAZIN-COMPOUNDS.

Phenyl-hydrazin, $C_6H_8N_2 = C_6H_5—NH—NH_2$.—When diazobenzene nitrate is added to a cold solution of acid potassium sulphite, the liquid solidifies to yellow crystals of potassium diazobenzene sulphonate, $C_6H_5N_2SO_3K$ or $C_6H_5—N{=}N—SO_3K$; this salt, heated on the water-bath with excess of acid potassium sulphite, is converted into colourless phenyl hydrazinsulphonate, $C_6H_5—NH—NH—SO_3K$, which is also formed by heating the former salt with zinc-dust and hydrochloric acid; and this colourless salt heated with hydrochloric acid yields the hydrochloride of phenyl-hydrazin, according to the equation:

$$C_6H_5.N_2H_2.SO_3K + HCl + H_2O = C_6H_5.N_2H_3.HCl + SO_4KH.$$

It is more easily obtained (together with aniline or diethylamine), by treating an alcoholic solution of diazo-amidobenzene or diazobenzene-diethylamine with zinc-dust and acetic acid.

Phenylhydrazin is a yellow oil, which solidifies at low temperatures to a crystalline mass, melting at 23°, and boiling at 233°–234°. It dissolves sparingly in cold water, more readily in hot water, very easily in alcohol and ether. It possesses strong reducing properties, and is a mono-acid base, forming well-crystallised salts. Its hydrochloride, treated with potassium nitrite, yields the nitroso-compound $C_6H_5.N(NO).NH_2$, which, when heated with water, is converted into diazobenzenimide, $C_6H_5N_3$. The nitroso-compound, treated with phenol and strong sulphuric acid, yields a brown solution, changing to green and blue (Liebermann's reaction, p. 480).

SULPHO-DERIVATIVES.

The sulpho-acids of the aromatic hydrocarbons are easily formed by the direct action of sulphuric acid, concentrated or fuming, on these hydrocarbons; thus:

$$C_6H_6 + SO_4H_2 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5.SO_3H} + H_2O;$$

$$C_6H_6 + 2SO_4H_2 = \underset{\text{Benzene-disulphonic acid.}}{C_6H_4(SO_3H)_2} + 2H_2O.$$

In this respect they differ from the sulpho-acids of the fatty group, which can be formed only from sulphites or from thio-alcohols (p. 113).

The aromatic hydrocarbons treated with sulphuric anhydride yield sulphoxides:

$$2C_6H_6 + SO_3 = \underset{\text{Benzene-sulphoxide.}}{(C_6H_5)_2SO_2} + H_2O.$$

The sulpho-acids treated with phosphorus pentachloride, or their salts treated with the oxychloride, yield the sulphochlorides or chloranhydrides of the sulphonic acids; *e.g.*,

$$C_6H_5.SO_2.OH + PCl_5 = C_6H_5.SO_2.Cl + POCl_3 + HCl;$$

$$3(C_6H_5.SO_2.OK) + POCl_3 = 3(C_6H_5.SO_2.Cl) + PO_4K_3;$$

and the sulphochlorides treated with sodium-amalgam in ethereal solution, are converted into sulphinic acids (p. 114):

$$C_6H_5.SO_2.Cl + H_2 = C_6H_5.SO_2H + HCl.$$

The sulphinic acids, or rather their zinc-salts, are also formed by the action of the zinc-compounds of the alcohol-radicles on the sulpho-chlorides; *e.g.*,

$$2(C_6H_5.SO_2.Cl) + Zn(C_2H_5)_2 = 2C_2H_5Cl + (C_6H_5SO_2)_2Zn.$$

By zinc and hydrochloric acid, on the other hand, the sulphochlorides are reduced to hydrosulphides or thiophenols:

$$C_6H_5.SO_2Cl + 3H_2 = C_6H_5.SH + 2H_2O + HCl.$$

The aromatic sulpho-acids, like those of the fatty group, are very stable compounds, not decomposed by boiling with alkalis. By fusion with caustic alkalis they yield phenols:

$$C_6H_5.SO_3K + KHO = C_6H_5.OH + SO_3K_2.$$

By distillation with *potassium cyanide* (or the dry ferrocyanide), they yield nitrils:

$$C_6H_5.SO_3K + CNK = C_6H_5.CN + SO_3K_2.$$

The free acids subjected to dry distillation yield hydrocarbons; benzene-sulphoxide, or its homologues, being formed at the same time; thus:

$$C_6H_5.SO_3H = C_6H_6 + SO_3,$$

and

$$2C_6H_6 + SO_3 = (C_6H_5)_2SO_2 + H_2O.$$

The sulphonic acids of the substituted hydrocarbons are obtained by the action of sulphuric acid on these bodies, or by the action of halogens, or of nitric acid, on the sulpho-acids of the primary hydrocarbons; in the latter case the sulpho-group is also frequently replaced. The sulpho-group may also be replaced by chlorine, by heating a sulpho-acid or sulphochloride with phosphorus pentachloride:

$$C_6H_4Cl.SO_2Cl + PCl_5 = C_6H_4Cl_2 + POCl_3 + SOCl_2.$$

Benzenesulphonic Acid, $C_6H_5.SO_3H$, is produced by heating benzene with an equal weight of ordinary sulphuric acid. On diluting the resulting solution with water, neutralising with barium or lead carbonate, decomposing the resulting barium or lead-salt with sulphuric acid, or hydrogen sulphide, and evaporating the filtrate to the crystallising point, benzenesulphonic acid is obtained in small deliquescent tabular crystals, containing $C_6H_5.SO_3H + 1\frac{1}{2}H_2O$, easily soluble in water and in alcohol. By dry distillation it yields benzene; by fusion with potash, phenol. Its *barium salt*, $(C_6H_5SO_3)_2Ba + H_2O$, forms nacreous plates, easily soluble in water. The *zinc-salt*, $(C_6H_5SO_3)_2Zn + 6H_2O$, crystallises in six-sided tables. The *ethylic ether*, $C_6H_5SO_3.C_2H_5$, obtained by heating the lead salt to 100° with ethyl iodide, forms slender needles, decomposed by boiling with water.

Benzene-sulphochloride, $C_6H_5.SO_2Cl$, separates, on gently warming an intimate mixture of sodium benzenesulphonate and phosphorus pentachloride, and then shaking it up with water, as a colourless oil having a specific gravity of 1·378 at 23°, boiling with partial decomposition at 246°–247°, and solidifying below 0° in large rhombic crystals. Boiling water slowly decomposes it into benzenesulphonic and hydrochloric acids.

Benzenesulphamide, $C_6H_5.SO_2.NH_2$, formed by treating the sulphochloride with ammonia or ammonium carbonate, crystallises from alcohol in nacreous laminæ melting at 149°. Silver nitrate added to its alcoholic solution throws down the compound $C_6H_5SO_2.NHAg$.

Benzenesulphinic or **Benzenesulphurous Acid,** $C_6H_5.SO_2.OH$ formed by the action of sodium-amalgam on the ethereal solution of benzenesulphonic acid, crystallises from hot water in large shining prisms, easily soluble in alcohol and ether, melting at 69°, and decomposing at 100°. With chlorine or bromine it forms benzenesulphochloride or bromide, and is converted, slowly by exposure to the air, quickly by oxidising agents, into benzenesulphonic acid. The *silver salt*, $C_6H_5.SO_2.Ag$, is slightly soluble in water.

Phenyl Sulphoxide or **Sulphobenzide,** $(C_6H_5)_2S_4O_2$, is formed by dry distillation of benzenesulphonic acid, by oxidation of phenyl sulphide, $(C_6H_5)_2S$, and by the action of fuming sulphuric acid or sulphuric anhydride on benzene. It is very slightly soluble in water, crystallises from alcohol in plates, melts at 128°–129°, and distils without decomposition. By heating with strong sulphuric acid, it is converted into benzenesulphonic acid, $(C_6H_5)_2SO_2 + SO_4H_2 = 2(C_6H_5.SO_3H)$; and when heated with phosphorus pentachloride or in a stream of chlorine, it is decomposed, with formation of chlorobenzene and benzenesulphochloride:

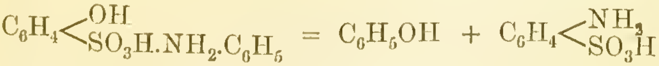
$$(C_6H_5)_2SO_2 + Cl_2 = C_6H_5Cl + C_6H_5.SO_2Cl.$$

The action of chlorine in sunshine also converts it into chlorobenzene and its products of addition.

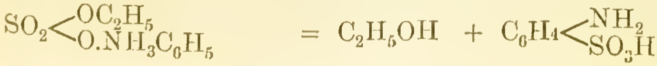
Phenyldisulphoxide, $(C_6H_5)_2S_2O_2$, produced, together with benzenesulphonic acid, by heating benzenesulphinic acid with water to 130°, crystallises in long shining needles, melting at 100°, insoluble in water, easily soluble in alcohol and ether.

Chloro-, Bromo-, Iodo-, Nitro-, and **Amido-benzenesulphonic Acids,** $C_6H_4Cl.SO_3H$, &c.—The sulpho-acids formed by dissolving C_6H_5Cl, C_6H_5Br, C_6H_5I, and $C_6H_5NH_2$, in slightly fuming sulphuric acid, belong chiefly to the para-series (1 : 4), *e.g.*, $C_6.SO_3H.H.H.Br.H_2$; nitrobenzene, on the other hand, yields by similar treatment a product consisting also wholly of *meta*-nitrobenzenesulphonic acid, $C_6.SO_3.H.NO_2.H_3$. The action of bromine or nitric acid on benzenesulphonic acid yields likewise a product consisting chiefly of the meta-acid. All these bodies are strong monobasic acids, which mostly crystallise well, dissolve easily in water, and yield well-crystallised salts, chlorides, and amides.

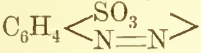
Para-amidobenzenesulphonic acid, long known by the name of sulphanilic acid, is produced by the action of sulphuric acid on aniline, also by distillation of phenolsulphate or of ethylsulphate of aniline:

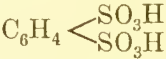


$$C_6H_4{<}\begin{matrix}OH\\SO_3H.NH_2.C_6H_5\end{matrix} = C_6H_5OH + C_6H_4{<}\begin{matrix}NH_2\\SO_3H\end{matrix}$$



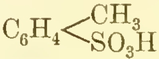
$$SO_2{<}\begin{matrix}OC_2H_5\\O.NH_3C_6H_5\end{matrix} = C_2H_5OH + C_6H_4{<}\begin{matrix}NH_2\\SO_3H\end{matrix}$$

It crystallises from water in rhombic tables containing one mol. H_2O; yields, by oxidation with chromic acid or with manganese dioxide and sulphuric acid, a large quantity of quinone, $C_6H_4O_2$; and is converted by nitrous acid into diazobenzene-sulphonic acid,  $C_6H_4\begin{matrix}<\\ \end{matrix}\!\!\begin{matrix}SO_3\\ N=N\end{matrix}\!\!>$, which crystallises from hot water in colourless needles; detonates with great violence, and is converted into benzenesulphonic acid by heating with absolute alcohol, and into sulphanilic acid by the action of hydrogen sulphide.

Benzenedisulphonic Acids,  $C_6H_4<\begin{matrix}SO_3H\\ SO_3H\end{matrix}$.—The *meta-* and *para*-modifications of this acid are obtained by heating benzenesulphonic acid with fuming sulphuric acid, or more readily by passing benzene vapour into ordinary sulphuric acid heated to 240°. They are both very soluble in water, but may be separated by fractional crystallisation of their potassium salts. The *meta*-acid, which is the principal product, yields a chloride, $C_6H_4(SO_2Cl)_2$, melting at 63° and an amide, $C_6H_4(SO_2.NH_2)_2$, melting at 229°. By distillation with potassium cyanide, it yields a dicyanide, $C_6H_4(CN)_2$, melting at 156°, and convertible by the action of alkalis into metaphthalic or isophthalic acid, $C_6H_4(CO_2H)_2$.

Parabenzenedisulphonic acid forms a chloride melting at 131°, and an amide melting at 288°. By distillation with potassium cyanide it yields a dicyanide, melting at 222°, and convertible into terephthalic acid, $C_6H_4(CO_2H)_2$ (1:4).

Benzenetrisulphonic Acid, $C_6H_3(SO_3H)_3$.—The only known modification of this acid is obtained by heating a mixture of 10 parts benzene, 70 fuming sulphuric acid, and 40 phosphoric anhydride in sealed tubes to 280°–290°. Separated from its lead salt by hydrogen sulphide, it crystallises in long flat needles containing 3 mol. H_2O.*

Toluenesulphonic Acids,  $C_6H_4<\begin{matrix}CH_3\\ SO_3H\end{matrix}$.—The *para-* and *ortho*-modifications are produced simultaneously by dissolving toluene in slightly fuming sulphuric acid, and may be approximately separated by fractional crystallisation of their potassium salts, the para-salt separating out first, and crystallising easily in large transparent six-sided tables or prisms containing 1 mol. H_2O. The *ortho*-salt separates from the mother-liquor mixed with para-salt, from which it is not easily purified. The *para*-acid crystallises in deliquescent scales containing 1 mol. H_2O. Its *chloride*, $C_7H_7(SO_2Cl)_2$, melts at 69°. The *amide*, $C_7H_7(SO_2NH_2)_2$ at 137°. Fused with potash it yields paracresol, $C_6H_4(CH_3).OH$, and a small quantity of paraoxybenzoic acid.—The *ortho*-acid, which may be obtained pure by decomposing its amide with nitrous acid, is liquid. Its amide crystallises from hot alcohol in shining octohedrons, melting at 153°–154°. The acid fused with potash yields ortho-cresol and ortho-oxybenzoic (salicylic) acid.

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* Koerner e Monselise, Gazzetta chimica italiana, 1876, p. 133.

Metatoluenesulphonic acid, $C_6.CH_3.H.SO_3H.H_3$, is obtained by the action of sodium-amalgam on the orthochloro- (or bromo-) toluenesulphonic acid, $C_6.CH_3.Br.SO_3H.H_2$, which is formed by dissolving orthochloro- (or bromo-) toluene in sulphuric acid. It is crystalline. Its *chloride* is a liquid not solidifying at –10° ; the *amide* is crystalline, and melts at 91°–92°.

A large number of substituted toluenesulphonic acids have been obtained by dissolving chlorotoluene, bromotoluene, &c., in sulphuric acid. Para- and ortho-toluenesulphonic acid heated with fuming sulphuric acid yield two modifications of toluenedisulphonic acid, $C_6H_3(SO_3H)_2.CH_3$.

Benzylsulphonic Acid, $C_6H_5.CH_2(SO_3H)$.—The potassium-salt of this acid is formed by heating benzyl chloride with a strong solution of potassium sulphite.

AROMATIC ALCOHOLS.

The substitution of OH for H in benzene gives rise to mono-, di-, and tri-atomic derivatives of alcoholic character, viz. :

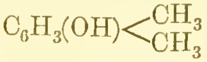
$$C_6H_5(OH) \qquad C_6H_4(OH)_2 \qquad C_6H_3(OH)_3.$$

In toluene and the higher homologues of benzene the substitution may take place either in the principal or in the lateral chains, giving rise to metameric compounds: thus from toluene, $C_6H_5.CH_3$, are derived

$C_6H_4(OH).CH_3$
Cresol.

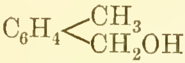
$C_6H_5.CH_2OH$,
Benzyl alcohol.

and from xylene, $C_6H_4(CH_3)_2$:



$$C_6H_3(OH)<\begin{matrix}CH_3\\CH_3\end{matrix}$$

Xylenol.



$$C_6H_4<\begin{matrix}CH_3\\CH_2OH\end{matrix}$$

Xylyl alcohol.

Those compounds in which the substitution takes place in the lateral chains, are primary alcohols, containing the group CH_2OH, and, like the corresponding alcohols of the fatty series, are convertible by oxidation into aldehydes and acids containing the same number of carbon-atoms, and readily exchange their OH group for Cl, Br, NH_2, &c., giving rise to haloïd derivatives and amines. Those, on the other hand, in which the OH is situated in the principal chain, are not convertible by oxidation into aldehydes, ketones, or acids, in which respect they are analogous to the tertiary alcohols.

These latter compounds, including the hydroxyl-derivatives of benzene, are called Phenols. They are susceptible of isomeric modifications, according to the orientation of the substituted radicles in the benzene-nucleus.

Monatomic Phenols.

These compounds are produced: 1. By the action of nitrous acid on aniline and its homologues in aqueous solution:

$$C_6H_5.NH_2 + NO.OH = C_6H_5.OH + H_2O + N_2.$$

2. By decomposing the diazo-compounds with water, the sulphates being the best adapted for the purpose (p. 469).

3. By fusing the aromatic sulphonic acids with caustic alkalis:

$$C_6H_4 < {CH_3 \atop SO_3K} + KOH = SO_3K_2 + C_6H_4 < {CH_3 \atop OH}.$$

Toluene-sulphonate. Cresol.

4. By distilling the salts of aromatic oxy-acids with lime.

$$C_6H_4(OH).CO_2H = CO_2 + C_6H_5.OH.$$

Oxybenzoic acid. Phenol.

5. By the dry distillation of complex organic substances, such as wood and coal.

The phenols exhibit acid as well as alcoholic characters. When treated with metallic oxides, especially those of the alkali-metals, they readily exchange their hydroxylic hydrogen for metals, forming metallic salts, and these, when acted upon by alcoholic iodides, are converted into phenolic ethers; *e.g.*,

$$C_6H_5.OK + CH_3I = KI + C_6H_5.O.CH_3.$$

Potassium phenate. Methyl-phenol.

Phenolic ethers containing acid radicles, such as $C_6H_5.O.OC_2H_3O$, are formed by the action of the chlorides of such radicles on the phenols and their metallic derivatives.

By the action of the halogen-compounds of phosphorus, the phenols are converted, by exchange of their OH-group for Cl, Br, &c., into halogen-derivatives of hydrocarbons, such as C_6H_5Cl. By phosphorus pentasulphide, they are converted into thiophenols:

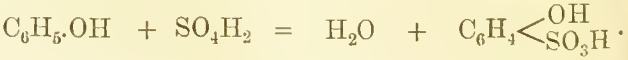
$$5C_6H_5(OH) + P_2S_5 = P_2O_5 + 5C_6H_5(SH).$$

By heating with zinc-dust they are reduced to hydrocarbons.

By treatment with chlorine, bromine, iodine, nitric acid, and sulphuric acid, the phenols are converted into halogen-, nitro-, and sulpho-derivatives, by exchange of one or more atoms of hydrogen in the benzene-nucleus for Cl, Br, I, NO_2, or SO_3H; thus:

$$C_6H_6OH + Cl_2 = HCl + C_6H_4Cl.OH.$$

Chlorophenol.



$$C_6H_5.OH + SO_4H_2 = H_2O + C_6H_4 < {OH \atop SO_3H}.$$

Phenolsulphonic acid.

Phenols treated with metallic sodium and carbon dioxide are converted into salts of aromatic oxy-acids:

$$\underset{\text{Phenol.}}{C_6H_5.OH} + CO_2 = \underset{\text{Oxybenzoic acid.}}{C_6H_4(OH).CO_2H}.$$

The monatomic phenols at present known contain 6, 7, 8 and 10 atoms of carbon.

Six-carbon Phenol, or simply **Phenol,** $C_6H_6O = C_6H_5OH$. —*Phenyl alcohol, Phenic acid, Carbolic acid, Coal-tar creasote.*—This compound is produced: 1. By the action of nitrous acid on aniline.

2. By the dry distillation of salicylic (ortho-oxybenzoic)) acid. It may be conveniently prepared by heating crystallised salicylic acid strongly and quickly in a glass retort, either alone or mixed with pounded glass or quicklime. Phenol then passes over into the receiver, and crystallises almost to the last drop.

3. Phenol is produced in the dry distillation of coal, and forms the chief constituent of the acid portion of coal-tar oil; this is the source from which it is most frequently obtained. Crude coal-tar oil is agitated with a mixture of slaked lime and water, the whole being left for a considerable time; the aqueous liquid separated from the undissolved oil is decomposed by hydrochloric acid, and the oily product thus obtained is purified by cautious distillation, the first third only being collected. Or the coal-tar oil is subjected to distillation in a retort furnished with a thermometer, and the portion which passes over between the temperature of 150° and 200° is collected apart. This product is then mixed with a hot, strong solution of caustic potash, and left to stand, whereby a whitish, somewhat crystalline, pasty mass is obtained, which, by the action of water, is resolved into a light oily liquid and a dense alkaline solution. The latter is withdrawn by a siphon, decomposed by hydrochloric acid, and the separated oil purified by contact with calcium chloride, and redistillation. Lastly, it is exposed to a low temperature, and the crystals formed are drained from the mother-liquid, and carefully preserved from the air.

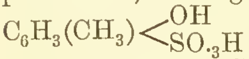
Pure phenol crystallises in long colourless prismatic needles, having a specific gravity of 1·066, melting at 40°–41°, and boiling at 181·5°: the commercial product forms a crystalline mass, which turns reddish in a short time, and in contact with moist air deliquesces to a brown liquid. Phenol has a penetrating odour, a strong burning taste, and attacks the skin of the lips. It is poisonous, exerts an antiseptic action, and has been successfully used by Mr. Crookes for destroying the infection of cattle-plague. It dissolves in about 15 parts of water at ordinary temperatures, very easily in alcohol and ether. Sulphur and iodine dissolve in it; nitric acid, chlorine, and bromine attack it with energy, forming substitution-products, all of which are of acid character. With strong sulphuric acid, it forms phenolsulphonic acid, $C_6H_4(OH).SO_3H$. The aqueous solution is coloured violet by ferric chloride, and stains a deal shaving of a fine blue colour. With bromine-water, even when very dilute, it forms a white precipitate of tribromophenol.

On adding phenol to nitric acid containing nitrous acid, or to a solution of potassium nitrite (6 per cent.) in strong sulphuric acid, a brown colour is produced, changing to green, and ultimately to a fine blue (Liebermann's reaction). Fine colours are produced in like manner with other phenols, mono- and poly-atomic; also by phenols in presence of sulphuric acid with diazo- and nitroso-compounds.

PHENATES.—Phenol dissolves in alkalis, forming salts which are difficult to obtain in definite form. *Potassium phenate*, C_6H_5KO, obtained by heating phenol with potassium, or with solid potassium hydroxide, crystallises in slender white needles. On heating this potassium-compound with iodide of methyl, ethyl, or amyl, ethers are produced—viz., methyl phenate or anisol, $C_6H_5OCH_3$; ethyl phenate or phenetol, $C_6H_5OC_2H_5$, and amyl phenate or phenamylol, $C_6H_5OC_5H_{11}$. These bodies resemble the mixed ethers of the ordinary alcohols (p. 110) in composition and mode of formation, but differ greatly from them in their behaviour with sulphuric and nitric acids, with which in fact they behave just like phenol itself, forming substitution-products possessing acid properties.

Methyl Phenate or Anisol, $C_7H_8O = C_6H_5.O.CH_3$, is also produced, with evolution of carbon dioxide, by distilling methyl-salicylic acid or anisic (methyl-paraoxybenzoic) acid with baryta:

$$C_6H_4(OCH_3).CO_2H = CO_2 + C_6H_5.O.CH_3.$$

Anisol is a colourless, very mobile liquid, having a pleasant aromatic odour, a density of 0·991 at 15°, and boiling without decomposition at 152°. It dissolves completely in strong sulphuric acid, forming methylphenol-sulphonic or sulphanisolic acid,  $C_6H_3(CH_3)<\begin{matrix}OH\\SO_3H\end{matrix}$.—With *bromine* it forms three substitution-products — viz., $C_6H_4Br.O.CH_3$, a liquid boiling at 223°; $C_6H_3Br_2.O.CH_3$, which crystallises in rhombic tables, melts at 59°, and boils at 272°; and $C_6H_2Br_3.O.CH_3$, which melts at 87°, and is sublimable. By the further action of bromine, tetrabromoquinone or bromanil, $C_6Br_4O_2$ is produced. Fuming nitric acid acts strongly on anisol, forming the three nitranisols, $C_7H_7(NO_2)O$, $C_7H_6(NO_2)_2O$, and $C_7H_5(NO_2)_3O$, which, when treated with reducing agents, yield the corresponding nitranisidines $C_7H_5(NH_2)O$, &c.

Ethyl Phenate or Phenetol, $C_6H_5.O.C_2H_5$, obtained from phenol, and from ethylsalicylic acid, is an aromatic liquid, boiling at 172°.—Amyl Phenate or Phenamylol boils at 225°.

Ethene Phenate, $C_2H_4(OC_6H_5)_2$, produced by the action of ethene bromide on potassium phenate, crystallises in laminæ melting at 95°.

Phenyl Phenate, Phenyl Oxide, or Phenolic Ether,

$C_{12}H_{10}O = (C_6H_5)_2O$, formed, together with phenyl benzoate, by the dry distillation of cupric benzoate, and by heating diazobenzene sulphate with phenol: crystallises in long needles, melts at 28° and boils at 246°; dissolves easily in alcohol and ether.

Thiophenol or Phenyl Hydrosulphide, $C_6H_5.SH$, formed by the action of P_2S_5 on phenol, and by that of nascent hydrogen (zinc and sulphuric acid) on phenyl-sulphochloride, is a colourless, mobile, fetid liquid, having a density of 1·078 at 14°, and boiling at 168°. It is insoluble in water, but dissolves easily in alcohol and ether, and the alcoholic solution is precipitated by silver, lead, and mercury salts, yielding compounds analogous to the mercaptides. The mercury-compound, $(C_6H_5S)_2Hg$, crystallises from alcohol in shining needles.

Phenyl Sulphide, $(C_5H_5)_2S$, produced by the dry distillation of sodium benzene-sulphonate, and, together with the hydrosulphide, by the action of P_2S_5 on phenol, is a colourless liquid, having an alliaceous odour, a density of 1·12, and boiling at 292°. Nitric acid oxidises it to phenyl sulphoxide (sulphobenzide) $(C_6H_5)_2SO_2$.

Phenyl Disulphide, $(C_6H_5)_2S_2$ is formed by oxidising thiophenol with dilute nitric acid, and by the action of iodine on the aqueous solution of potassium-thiophenol:

$$2(C_6H_5.SK) + I_2 = 2KI + (C_6H_5)_2S_2.$$

It crystallises from alcohol in shining needles melting at 60°; is oxidised by nitric acid to benzenesulphonic acid, and reduced by nascent hydrogen to thiophenol.

Halogen Derivatives of Phenol.

Chlorophenols.—The three monochlorophenols, $C_6H_4Cl.OH$, *ortho-*, *meta-*, and *para-*, are formed from the corresponding chloranilines (p. 449), by the diazo-reaction. The ortho- and para-compounds are also produced by passing chlorine into warm phenol, and may be separated by fractional distillation. (1 : 2) *Chlorophenol* is a colourless liquid, boiling at 175°–176°, solidifying at $-12°$; converted by fusion with potash into pyrocatechin. (1 : 3) *Chlorophenol*, from (1 : 3) chloraniline, is a liquid boiling at 214°. (1 : 4) *Chlorophenol* crystallises in colourless prisms, which gradually turn red, melts at 37°, boils at 217°; is converted by fusion with potash into hydroquinone. All the three chlorophenols have a very pungent and persistent odour.

Dichlorophenol, $C_6H_3Cl_2.OH$, probably $C_6.OH.Cl.H.Cl.H_2$, obtained by dry distillation of dichlorosalicylic acid, melts at 43°, and boils at 209°.—*Trichlorophenol*, $C_6H_2Cl_3.OH$ (1 : 3 : 5, OH), the chief product of the action of chlorine on phenol, melts at 68°, and boils at 244°.—*Pentachlorophenol*, $C_6Cl_5.OH$, obtained by the action of chlorine on phenol, in presence of antimonic chloride, melts at 187°.

Bromophenols.—The three monobromophenols, $C_6H_4Br.OH$, are obtained from the three corresponding bromanilines; the 1 : 2 and 1 : 4 modifications also, by passing bromine vapour into phenol, and by the action of bromine on a solution of phenol in glacial acetic acid. The *ortho-* and *meta-*modifications are liquid.—*Parabromophenol* forms large crystals; melts at 64°; boils at 236°; and is converted, by the action of phosphorus pentabromide, into paradibromobenzene.

Dibromophenol, $C_6H_3Br_2.OH$ (probably 1 : 2 : 4, OH in 1), obtained by bromination of phenol, melts at 40°.

Tribromophenol, $C_6H_2Br_3.OH$ (1 : 3 : 5, OH), precipitated by bromine-water from the aqueous solution of phenol, crystallises from alcohol in silky needles, melting at 95°. By PBr_5 it is converted into tetrabromobenzene, melting at 98° (p. 437); by nitric acid into picric acid.

Pentabromophenol, $C_6Br_5.OH$, melts at 225°.

Iodophenols.—The three monoiodophenols, $C_6H_4I.OH$, are formed, together with tri-iodophenol, by treating phenol with iodine and iodic acid in presence of free alkali:

$$5(C_6H_5.OH) + 2I_2 + IO_3H = 3H_2O + 5(C_6H_4I.OH).$$

On supersaturating the liquid with hydrochloric acid, and distilling the precipitated oil with steam, a liquid monoiodophenol (1 : 2) passes over first, then a solid (1 : 3), and finally, tri-iodophenol; and the residue contains a considerable quantity of the latter, which may be extracted by alcohol. The third monoiodophenol (1 : 4), which is easily soluble in water, is found partly in the aqueous solution from which the crude iodophenol has been precipitated, partly in the aqueous distillate, and partly in the alcoholic solution from which the tri-iodophenol has crystallised.

(1 : 2) Iodophenol, produced also from (1 : 2) amidophenol, and by distillation of iodosalicylic acid, is a liquid which does not solidify at −23°. It is easily decomposed, with separation of iodine, by chlorine and by nitric acid. By fusion with potash it yields pyrocatechin. (1 : 3) Iodophenol, produced also from metaiodaniline, is somewhat sparingly soluble in water, crystallises from alcohol in six-sided tables melting at 89°; is not decomposed either by chlorine or by nitric acid. By fusion with potash it yields resorcin. (1 : 4) Iodophenol, obtained also from para-iodaniline, is very soluble in water, crystallises in shining needles melting at 64°–66°; is decomposed by nitric acid, but not by chlorine; converted by fusion with potash at 100° into hydroquinone.

Nitrosophenol, $C_6H_4(NO).OH$ (1 : 4).—This compound is formed: 1. By the action of nitrous acid on phenol:

$$C_6H_5.OH + NO.OH = H_2O + C_6H_4(NO).OH;$$

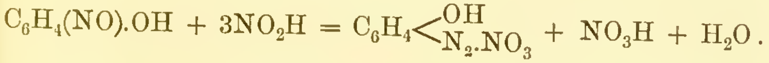
2. As a sodium salt, by heating nitrosodimethylaniline (p. 451) with dilute soda-ley :

$$C_6H_4(NO).N(CH_3)_2 + NaOH = NH(CH_3)_2 + C_6H_4(NO).ONa.$$

Pure hydrochloride of nitrosodimethylaniline is added to a boiling dilute solution of caustic soda; the dimethylaniline is distilled off; and the residue, acidified with dilute sulphuric acid, is shaken up with ether.

Nitrosophenol crystallises from hot water in slender colourless needles, which soon turn brown; from ether in large brown laminæ. It dissolves with light green colour in water, alcohol, and ether; easily also in dilute soda-ley, forming a sodium salt, which, on addition of strong caustic soda, separates in red needles containing $C_6H_4(NO).ONa + 2H_2O$. Salts of the heavy metals added to this solution throw down amorphous dark-coloured precipitates.

Nitrosophenol melts when heated, and decomposes with a slight explosion at 120°–130°. By strong nitric acid it is converted into paranitrophenol; by tin and hydrochloric acid into paramidophenol; by nitrous acid into diazobenzene nitrate :



$$C_6H_4(NO).OH + 3NO_2H = C_6H_4{<}^{OH}_{N_2.NO_3} + NO_3H + H_2O.$$

With aniline acetate it yields diazoxybenzene, $C_6H_4(OH).N_2.C_6H_5$.

On adding strong sulphuric acid to nitrosophenol dissolved in phenol, the solution assumes a dark red colour, changing, on addition of potash, to a fine blue.

Nitrophenols.

These compounds, which are all of acid character, are easily formed by direct nitration of phenol.

Mononitrophenols, $C_6H_4(NO_2).OH$, (1 : 2) and (1 : 4), are obtained by gradually adding 1 part of phenol to 2 parts of nitric acid (sp. gr. 1·34), dissolved in 4 parts of water. They may be separated by distillation with water, as only the ortho-compound volatilises with the steam. The same compounds are produced by heating (1 : 2) and (1 : 4) nitrobromobenzene in sealed tubes with alcoholic ammonia. The (1 : 4) and (1 : 3) compounds may be prepared by boiling the diazonitrobenzene nitrates from (1 : 4) and (1 : 3) nitroaniline with water; the (1 : 4) compound also by boiling paranitraniline with very strong solution of caustic soda.

(1 : 2), commonly called *volatile nitrophenol*, crystallises in large yellow prisms; dissolves sparingly in water, easily in alcohol, and volatilises easily with vapour of water; melts at 45°, and boils at 214°; converted by PCl_5 into (1 : 2) chloronitrobenzene. Its sodium salt, $C_6H_4(NO_2).ONa$, crystallises in dark red anhydrous prisms, and the methylic ether, $C_6H_4(NO_2).OCH_3$, formed from it by the action of methyl iodide, melts at 9°, and boils at 265°.

(1 : 3) Nitrophenol forms colourless needles, moderately soluble in water, melting at 96°.

(1 : 4) Nitrophenol forms long, colourless needles, melting at 115°, converted by PCl_5 into (1 : 4) chloronitrobenzene. Its methylic ether melts at 48°, boils at 260°, and is converted by heating with ammonia into (1 : 4) nitraniline.

Dinitrophenol, $C_6H_3(NO_2)_2.OH$ (1 : 2 : 4—OH in 1), is formed by the action of strong nitric acid on phenol and on *o*- and *p*-nitrophenol; also by boiling the corresponding dinitrochloro- or dinitro-bromobenzene (p. 444) with alkalis. Colourless plates, melting at 114°.

The *consecutive* modification (1 : 2 : 6—OH in 1), formed, together with the preceding from (1 : 2) nitrophenol, crystallises in needles melting at 63°–64°.

Both these compounds are converted by further nitration into picric acid.

Two other dinitrophenols, formed from (1 : 3) nitrophenol, the one melting at 104°, the other at 141°, are converted by further nitration into isopicric acid.

Trinitrophenols, $C_6H_3(NO_2)_3.OH$.—Two of these compounds are known. (1.) *Picric acid*, 1 : 2 : 4 : 6 (OH in 1), also called *Carbazotic acid*, is formed by nitration of phenol and of 1 : 2 : 4 and 1 : 2 : 6 dinitrophenol. It is also one of the ultimate products of the action of nitric acid upon indigo and numerous other substances, as silk, wool, several resins, especially that of *Xanthorrhœa hastilis* (yellow gum of Botany Bay), salicin and some of its derivatives, coumarin, &c. It is most economically prepared from phenol. One part of that substance is gradually added to strong nitric acid slightly warmed, and when the first violent reaction has subsided, three parts of fuming nitric acid are added, and the liquid is boiled till nitrous fumes are no longer evolved. The resinous mass thus produced is boiled with water; the resulting picric acid is converted into sodium-salt; and the solution mixed with sodium carbonate, which throws down the sodium picrate in crystals.

Picric acid crystallises in yellow shining prisms or laminæ, having an intensely bitter taste. It melts at 122·5°, sublimes when cautiously heated. It dissolves sparingly in cold water, more easily in hot water, still more in alcohol. It stains the skin deep yellow, and is used as a yellow dye for wool and silk. It is a strong acid, forming well-crystallised yellow salts, which detonate violently when heated, some of them also by percussion. The *potassium salt*, $C_6H_2(NO_2)_3.OK$, crystallises in long needles, very slightly soluble in water. The *sodium, ammonium,* and *barium salts* are easily soluble in water.

Methyl picrate, $C_6H_2(NO_2)_3.OCH_3$, formed by nitration of anisol (p. 480), crystallises in tables, which melt at 60° and sublime. *Ethyl picrate* forms colourless needles, which turn brown in the air, and melt at 78·5°.

Picrates of Hydrocarbons.—Picric acid affords characteristic reactions for the detection of certain hydrocarbons. For this purpose, it is convenient to use an alcoholic solution of the acid saturated at 20°–30°, and either—(1) add the hydrocarbon to the cold-saturated alcoholic solution; or (2) mix the picric acid solution with a hot alcoholic solution of the hydrocarbon; or (3) dissolve the hydrocarbon, with aid of heat, in the picric acid solution. The following combine under these circumstances with picric acid: *Naphthalene* is the only solid hydrocarbon whose cold-saturated alcoholic solution is precipitated by picric acid. The compound forms delicate stellate groups of yellow needles, easily soluble in alcohol. *Retene*, treated by method 2 or 3, forms similar needles of an orange-yellow colour. *Anthracene* also forms ruby-coloured needles still more soluble than the preceding; the red alcoholic solution is decolorised by addition of a little more alcohol. Other hydrocarbons contained in crude anthracene exhibit the same reaction, which appears to be peculiar to anthracene and its homologues. They may be distinguished from one another by the appearance of the precipitates under the microscope.

Picric acid is converted by PCl_5 into trinitrochlorobenzene, $C_6H_2(NO_2)_3Cl$, which is reconverted into picric acid by boiling with water. Picric acid distilled with calcium hypochlorite, or a mixture of potassium chlorate and hydrochloric acid, yields chloropicrin, $C(NO_2)Cl_3$; and with calcium hypobromite, bromopicrin, $C(NO_2)Br_3$ (p. 80).

Isopicric acid, $C_6H_2(NO_2)_3.OH$, formed by the action of fuming nitric acid on metanitrophenol, crystallises from hot water or from nitric acid in light yellow prisms melting at 174°. It stains the skin yellow.

Picrocyamic or *Isopurpuric acid*, $C_8H_5N_5O_6$, not known in the free state, is formed, as a potassium salt, $C_8H_4N_5O_6K$, by dropping a hot solution of picric acid (1 part in 9 of water) into a solution of potassium cyanide (2 parts CNK in 4 of water) heated to 60°. This salt crystallises in brown-red scales, having a green metallic lustre, sparingly soluble in cold water, dissolving in hot water and in alcohol with deep red colour (test for hydrocyanic acid and metallic cyanides). Detonates strongly when heated.

The dinitrophenols treated with potassium cyanide yield similar derivatives.

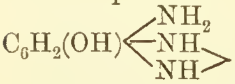
Nitrohaloïd derivatives of phenol, $C_6H_3Cl(NO_2).OH$, &c. are produced by the action of halogen elements on the nitrophenols.

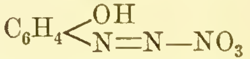
Amidophenols.

These compounds are formed by the action of reducing agents on the nitrophenols, the di- and tri-nitrophenols being partially reduce by alcoholic ammonium sulphide, completely by tin and hydrochloric acid. The entrance of the NH_2-group into the molecule considerably weakens the acid character of the compound, and when it replaces the whole of the nitro-groups, the compound becomes basic.

Monoamidophenols, $C_5H_4(NH_2).OH$.—The *ortho-* and *para-* compounds are formed by reduction of the corresponding nitro- or nitroso-compounds, best with tin and hydrochloric acid: the *p*-compound also by distillation of amidosalicylic acid.—(1:2) amidophenol forms colourless rhombic scales; (1:4) colourless needles, which soon turn brown. Both are slightly soluble in cold water, more easily in alcohol, and form well crystallised salts with acids; *o-* melts at 170°, *p-*, with decomposition, at 184°.

Amidonitrophenol or Picramic acid, $C_6H_2(NH_2)(NO_2)_2.OH$. —The ammonium salt of this acid, formed by passing hydrogen sulphide into an alcoholic solution of ammonium picrate, crystallises in red needles, and is decomposed by acetic acid, yielding the free acid, which also forms red needles melting at 165°.

Tri-amidophenol, $C_6H_2(NH_2)_3.OH$, is a triacid base not known in the free state. Its *hydriodide*, $C_6N_2(NH_2)_3OH.3HI$, obtained by the action of iodine and phosphorus on a hot saturated solution of picric acid, forms easily soluble colourless needles.—The *hydrochloride*, $C_6H_2(NH_2)_3OH.3HCl$, obtained by decomposing picric acid with tin and hydrochloric acid, and treating the resulting stannochloride, which separates on cooling, with hydrogen sulphide, crystallises in needles easily soluble in water, sparingly in strong hydrochloric acid. From these salts the base cannot be separated without decomposition. The solution of the hydrochloride mixed with ferric chloride acquires a deep blue colour, and if concentrated deposits the hydrochloride of amido-diimidophenol,  $C_6H_2(OH){<}\begin{matrix}NH_2\\ NH\\ NH\end{matrix}\!\!>$ in yellow-brown needles, having a blue shimmer in reflected light, and dissolving in water with a fine blue colour.

Diazophenol (*para*).—The *nitrate*,  $C_6H_4{<}\begin{matrix}OH\\ N{=}N{-}NO_3\end{matrix}$, is formed, together with *o-* and *p*-nitrophenol, by passing nitrous acid into an ethereal solution of phenol or nitrosophenol cooled with ice. It crystallises in light brown needles. The other salts of this base, which also crystallise well, are obtained by passing nitrous acid into the solutions of the corresponding salts of *p*-amidophenol. The salts of orthodiazophenol are obtained in like manner. All these salts are analogous in their reactions to the diazobenzene salts.

Phenol-sulphonic acids.

Phenol dissolves easily in strong sulphuric acid, forming *ortho-* and *para*-phenolsulphonic acid, $C_6H_4(OH).SO_3H$. At ordinary temperatures the *ortho*-acid is almost the only product, but it easily changes into the *para*-acid when heated. The two acids may be separated by fractional crystallisation of their potassium salts, the *p*- salt separating out first in elongated, hexagonal tables, which are anhydrous. The mother-liquors yield the *o*-salt in long, colourless spicules, containing $2H_2O$. Most of the other salts of the *p*-acid are less soluble than the corresponding *o*-salts. The two acids are not known in the free state. The sodium salt of the *p*-acid heated with MnO_2 and sulphuric acid yields quinone. Treated with PCl_5 it yields *p*-chlorophenol and *p*-dichlorobenzene. The *o*-acid fused with potash yields pyrocatechin; the *p*-acid, by molecular transformation, yields resorcin (see DIATOMIC PHENOLS).

Metaphenolsulphonic acid is formed as a potassium salt by heating potassium benzene-metadisulphonate dissolved in the smallest possible quantity of water, with two or three times its weight of potassium hydroxide for a considerable time to 170°–180°. The greater part of the potassium sulphate formed at the same time having been removed by crystallisation, the metaphenolsulphonate may be extracted from the mother-liquor by alcohol. This salt crystallises from water in groups of easily soluble efflorescent scales containing 1 mol. H_2O. The free acid forms concentric groups of very soluble needles. Ferric chloride colours the solutions of the three acids violet.

Phenoldisulphonic acid, $C_6H_3(OH)(SO_3H)_2$, is formed by heating phenol or *o*- or *p*-phenolsulphonic acid with excess of strong sulphuric acid, whence it has the structure 1:2:4 (OH in 1); also by the action of sulphuric acid on diazobenzene sulphate. The solutions of the acid and its salts are coloured dark red by ferric chloride.

Phenoltrisulphonic acid, $C_6H_2(OH)(SO_3H)_3$ (1:3:5, OH), formed by the action of strong sulphuric acid or phosphoric anhydride on phenol, crystallises in thick prisms containing $3\frac{1}{2}H_2O$.

Cresols, $C_7H_8O = C_6H_4{<}{CH_3 \atop OH}$.—*Tolyl alcohols.—Para-* and *ortho*-cresol occur in coal- and wood-tar, together with phenol, and may be separated from the latter by fractional distillation; but they cannot easily be separated one from the other. They are obtained in the pure state by fusing the potassium salts of the corresponding toluenesulphonic acids, $C_6H_4(CH_3)(SO_3H)$, with potash, or from the corresponding toluidines by the diazo-reaction (p. 470). They are converted into toluene by heating with zinc-dust, and into the corresponding oxytoluic or cresotic acids, $C_6H_3(CH_3)(OH)(CO_2H)$, by the action of sodium and carbon dioxide.

Orthocresol is likewise obtained, together with propene, by heating carvacrol (cymophenol), $C_{10}H_{14}O$, with phosphoric anhydride:

$$C_{10}H_{14}O = C_7H_8O + C_3H_6.$$

It is a colourless crystalline mass, melting at 31°–31·5°, boiling at 185°–186°; coloured blue by ferric chloride. By prolonged heating with potassium hydroxide it is converted into salicylic acid.

Metacresol, prepared from thymol, $C_{10}H_{14}O$, in the same manner as *o*-cresol from carvacrol, is a colourless liquid which smells like phenol, boils at 201°, remains liquid at the temperature of a mixture of solid carbon dioxide and ether, and is converted by fusion with potash into oxybenzoic acid. Its ethylic ether is an oil boiling at 190°.

Paracresol forms colourless prisms smelling like phenol, melting at 36°, and boiling at 198°. It dissolves sparingly in water, forming a solution which is coloured blue by ferric chloride. By fusion with potash, paracresol is converted into paraoxybenzoic acid. Its *ethylic ether* is an aromatic liquid boiling at 188°. The *methylic ether* boils at 174°, and is oxidised by chromic acid to methyl-paraoxybenzoic (anisic) acid, $C_6H_4(OCH_3)(CO_2H)$. The *acetic ether*, $C_7H_7.O.C_2H_3O$, is a liquid boiling at 208°–211°.

Nitro-cresols.—Several of these compounds are obtained by nitration of paracresol.—$C_7H_5(NO_2)_3O$, crystallises in yellow needles like picric acid.—$C_7H_6(NO_2)O$ obtained also by the action of nitrous acid on paratoluidine, is a dye-stuff, known as *Victoria yellow;* it forms yellow crystals, melting at 84°, less soluble in water than picric acid.

Thiocresols, or Tolyl Hydrosulphides, $C_6H_4<^{CH_3}_{SH}$, are produced from the three toluenesulphonic acids by reducing the corresponding chlorides, $C_6H_4(CH_3)(SOCl)$, with zinc and hydrochloric acid. *Ortho-*, shining laminæ, melting at 15°, boiling at 188°. *Meta-*, liquid, not solidifying at −10°. *Para-*, large laminæ, melting at 43°, boiling at 188°.

Eight-carbon Phenols, $C_8H_{10}O$.—This formula includes, two metameric phenols, viz.:

Dimethyl-phenol, ...	$C_6H_3(CH_3)_2OH$
Ethyl-phenol, ...	$C_6H_4(C_2H_5)OH$.

Two Dimethyl-phenols or Xylenols are produced by fusing the potassium-salt of xylenesulphonic acid, $C_8H_9SO_3K$, with potassium hydroxide. On decomposing the resulting mass with hydrochloric acid, digesting with ether, and distilling, a liquid passes over at 210°, which, when exposed to a winter temperature, separates into two isomeric modifications, one crystalline, the other liquid. The solid modification is likewise obtained by fusing the potassium-salt of oxymesitylenic acid with potash:

$$C_6H_2\left\{\begin{matrix}OK\\(CH_3)_2\\CO_2K\end{matrix}\right. + H_2O = CO_3K_2 + C_6H_3\left\{\begin{matrix}(CH_3)_2\\OH\end{matrix}\right..$$

Solid xylenol melts at 75° and boils at 216°; the liquid modification boils at 206·5°–208·5°.

A xylylic phenol is mentioned by Dr. Hugo Müller as occurring in coal-tar; this is probably also a dimethyl-phenol, inasmuch as products of destructive distillation have hitherto been found to yield only methyl-derivatives of benzene. The portion of aloïsol (a product obtained by distilling aloes with lime) which is soluble in potash, has the composition of a xylylic phenol, and is perhaps identical with the preceding. Creosote, from beech-tar, is a mixture of several phenols and their ethers, and usually consists of phenol, cresol, xylenol, guaiacol, $C_6H_4(OH)(OCH_3)$, and creosol, $C_6H_4(CH_3)(OH)(OCH_3)$.

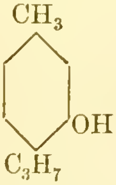
Ethyl-phenol, obtained from ethyl-benzenesulphonic acid, melts at 47°, boils at 211°, and volatilises even at ordinary temperatures.

Phlorol, an oily liquid obtained by the dry distillation of the barium salt of phloretic or oxethyl-benzoic acid, $C_9H_{10}O_3$ or $C_6H_4(OC_2H_5).COOH$, is also an ethyl-phenol, its formation being represented by the equation:

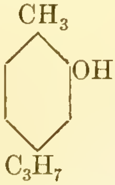
$$\underset{\text{Phloretic acid.}}{C_6H_4(OC_2H_5).COOH} = CO_2 + \underset{\text{Phlorol.}}{C_6H_5(OC_2H_5)}.$$

Phlorol is a colourless, strongly-refracting oil, having a specific gravity of 1·0374 at 12°, and boiling at 220°. It dissolves in strong sulphuric acid, forming a sulpho-acid which yields a soluble barium salt. With chlorine it forms a substitution-product. It reacts violently with strong nitric acid, forming the compound $C_8H_7(NO_2)_3O$. By sodium and carbon dioxide it is converted into phloretic acid.

Ten-Carbon Phenols, $C_{10}H_{13}.OH$.—Two compounds represented by this formula are known, viz.:—thymol and carvacrol. Both are methyl-propyl-phenols, $C_6H_3(CH_3)(C_3H_7)(OH)$, and have the methyl-group in the para-position relatively to the propyl-group; but in thymol the CH_3-group stands to the OH in the meta-position; in carvacrol in the ortho-position, thus:



Thymol.



Carvacrol.

Both are resolved by heating with phosphoric anhydride into propene, C_3H_6, and cresol, thymol yielding meta-, and carvacrol yielding ortho-cresol (p. 487).

Thymol exists, together with cymene, $C_{10}H_{14}$, and thymene, $C_{10}H_{16}$, in the volatile oils of thyme (*Thymus serpyllum*), horse-mint (*Mentha silvestris*), *Ptychotis Ajowan*, an East Indian plant, and *Monarda punctata*, or Oswego tea, a native of North America. It crystallises in large transparent plates, has a mild odour, a peppery taste, melts at 44°, and boils at 230°. Its *methylic ether* boils at 205°, the *ethylic ether* at 220°.

Thymol treated with *bromine* in sunshine yields pentabromothymol, $C_{10}H_9Br_5O$, and with *chlorine*, $C_{10}H_{11}Cl_3O$ or $C_{10}H_9Cl_5O$, accordingly as the reaction takes place in the shade or in sunshine; both of these, as well as the bromine-compound, are crystalline.

There are two nitrothymols, $C_{10}H_{12}(NO_2)_2O$ and $C_{10}H_{11}(NO_2)_3O$, obtained by the action of nitric acid on thymol-sulphonic acid. Both form potassium salts, which crystallise in yellow or orange-yellow needles.

Carvacrol, Oxycymene, or *Cymenol,* is obtained by fusing cymene-sulphonic acid, $C_{10}H_{13}.SO_3H$, with potash, and by heating camphor with one-fifth of its weight of iodine; also from the isomeric compound carvol, contained in oil of caraway (*Carum Carui*), by heating with phosphoric acid. It is a thick oil, not solidifying at -25°, boiling at 233°-235°.

Thymol and carvacrol distilled with phosphoric anhydride yield two isomeric thiophenols, $C_{10}H_{13}.SH$, both of which are non-solidifying liquids. Thiothymol boils at 230°-231°; thiocymenol at 235°.

Diatomic Phenols, $C_nH_{2n-8}(OH)_2$.

There are seven known compounds included in this formula, viz.:

Pyrocatechin—Resorcin—Hydroquinone, .	$C_6H_4(OH)_2$
Orcin—Homo-pyrocatechin, ...	$C_6H_3(CH_3)(OH)_2$
Beta-orcin—Hydrophlorone, . . .	$C_6H_2(CH_3)_2(OH)_2$.

These compounds are formed by the action of melting potash on the monohaloïd derivatives of the monatomic phenols, and on the phenolsulphonic acids:

$$C_6H_4Cl.OH + KOH = KCl + C_6H_4(OH)_2$$

$$C_6H_4(OH).SO_3K + KOH = SO_3K_2 + C_6H_4(OH)_2;$$

also on resins; and by the dry distillation of aromatic dioxyacids—such as oxysalicylic acid, $C_6H_3(OH)_2.CO_2H$, with lime or baryta:

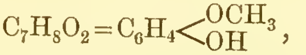
$$C_6H_3(OH)_2.CO_2H = CO_2 + C_6H_4(OH)_2.$$

Pyrocatechin, $C_6H_4(OH)_2$ (1:2), also called *Oxyphenic acid,* is formed: 1. By fusing orthochlor- or orth-iodophenol with potash.—2. By the dry distillation of oxysalicylic or of protocatechuic acid, $C_7H_6O_4$.—3. By dry distillation of catechin (the juice of *Mimosa Catechu*), from which it was first obtained; also from morintannic acid (the yellow colouring matter of *Morus tinctoria*); and of wood, whence it is found in wood-vinegar.—4. By heating its methylic ether (guaiacol) with hydriodic acid to 200°:

$$C_6H_4(OH)(OCH_3) + HI = CH_3I + C_6H_4(OH)_2.$$

This reaction affords the best method of preparing it.

Pyrocatechin crystallises in short square prisms; sublimes even at ordinary temperatures, in shining laminæ; melts at 104°, and boils at 245·5°. It dissolves easily in water, alcohol, and ether. The aqueous solution mixed with *ferric chloride* assumes a dark-green colour, changing to violet on addition of a small quantity of ammonia, acid sodium carbonate, or tartaric acid. Pyrocatechin reduces *silver nitrate* at ordinary temperatures, an ammoniacal solution of copper with the aid of heat. *Nitric acid* acts violently upon it, forming oxalic acid and a small quantity of a yellow nitro-compound. With *acetyl chloride* and *benzoyl chloride* it forms the compounds $C_6H_4(O.C_2H_3O)_2$ and $C_6H_4(O.C_7H_5O)_2$, both of which are crystalline. Its aqueous solution forms, with *lead acetate*, a white precipitate, $C_6H_4O_2Pb$.

Methyl-pyrocatechin or *Guaiacol*, 
$C_7H_8O_2 = C_6H_4 {<}^{OCH_3}_{OH}$, is one of the constituents of beech-tar creosote (p. 489), and may be separated therefrom by fractional distillation. It is produced by heating pyrocatechin with potassium hydroxide and potassium methylsulphate to 180°; by heating methyl-pyrocatechuic acid with calcium hydrate: $C_7H_5(CH_3)O_4 = CO_2 + C_6H_5(CH_3)O_2$; and by dry distillation of guaiac resin.

Guaiacol is a colourless liquid, having a specific gravity of 1·117, and boiling at 200°; slightly soluble in water, easily in alcohol, ether, acetic acid, and alkalis. It forms crystalline salts with the alkalis and alkaline earths, and its alkaline solutions reduce the salts of gold, silver, and copper. By heating with hydriodic acid or fusion with potash, it is resolved into pyrocatechin and methyl iodide or methyl alcohol.

Dimethyl-pyrocatechin, $C_6H_4(O.CH_3)_2$, formed by heating the potassium derivative of methyl-pyrocatechin with methyl iodide, is a liquid boiling at 205°.

Resorcin, $C_6H_4(OH)_2$ (1 : 3), is formed by the action of melting potash on the para-modifications of chlorophenol, iodophenol, chloro- and bromo-benzenesulphonic acids, phenolsulphonic and benzenedisulphonic acids; also on some compounds not belonging to the para- series. It appears indeed to be the most stable of the three diatomic phenols, and is accordingly produced by molecular transposition, especially at high temperatures, in some cases when an ortho- or para-compound might be expected to result. Resorcin is also formed by the action of melting potash on umbelliferone, and on various resins and gum-resins, as galbanum, assafœtida, gum ammoniacum, sagapenum, and acaroïd resin. It is most easily prepared by the dry distillation of extract of Brazil wood.

Resorcin is very soluble in water, alcohol, and ether, and crystallises from very concentrated solutions, in prisms belonging to the trimetric system, colourless at first, but afterwards becoming reddish. It melts at 110°, and boils at 271°, distilling almost without residue. Its aqueous solution is coloured violet by ferric chloride, is not precipitated by lead acetate, and reduces silver nitrate only at the boiling heat, except in presence of ammonia, in which case the reduction takes place in the cold. These characters distinguish resorcin from pyrocatechin. A very delicate test for resorcin is its conversion into fluorescein (*q. v.*) by heating with phthalic anhydride. Bromine-water added to the aqueous solution throws down the *tribromo-compound*, $C_6HBr_3(OH)_2$. Resorcin also forms a *triacetyl-compound*, $C_6H_3(C_2H_3O)(O.C_2H_3O)_2$, and two *benzoyl-derivatives*, $C_6.H_2(O.C_7H_5O)_2$, and $C_6H_3(C_7H_5O)(O.C_7H_5O)_2$.

Nitro-resorcins.—Di-nitroresorcin, $C_6H_2(NO_2)_2.(OH)_2$, formed by adding potassium nitrite to a very dilute solution of resorcin mixed with acetic acid, crystallises with molecules of water in yellowish grey or brown laminæ, which detonate when heated to 115°.

Trinitroresorcin, Oxypicric or *Styphnic acid*, $C_6H(NO_2)_3(OH)_2$, is produced by the action of cold nitric acid on several gum-resins (galbanum, sagapenum, gum ammoniacum), and on many vegetable extracts (Sapan-wood, Brazil-wood, &c.).; also by heating metanitrophenol with strong nitric acid. It crystallises in large yellow hexagonal prisms or laminæ, sparingly soluble in water, melting at 175°, and subliming when cautiously heated, exploding when quickly heated. With ferrous sulphate and lime-water, it exhibits at first a green colour, which afterwards disappears (distinction from picric acid, which is thereby coloured blood-red). Trinitroresorcin is a strong bibasic acid, forming well-crystallised salts, which detonate violently when heated.

Tri-amidoresorcin, $C_6H(NH_2)_3(OH)_2$.—The hydrochloride of this base, $C_6H_9N_3O_2.3HCl+H_2O$, produced by the action of tin and hydrochloric acid on trinitroresorcin, forms large yellowish, easily soluble crystals. The solution of the stanno-chloride (the immediate product of the reaction), is coloured dark red by ferric chloride, or by exposure to the air, and deposits on standing red needles, consisting of the hydrochloride of amido-diimido-resorcin, $C_6H(OH)_2(NH_2){<}\substack{NH\\NH}{>}.HCl$. Ammonia added to the solution of this salt separates the free base in slender needles, having a green metallic lustre.

Hydroquinone, $C_6H_4(OH)_2$ (1 : 4), is formed by fusing paraiodophenol with potash to 180°; by dry distillation of oxysalicylic and of quinic acid, and by heating the aqueous solution of the latter with lead peroxide:

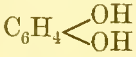
$$C_7H_{12}O_6 + O = C_6H_6O_2 + CO_2 + 3H_2O;$$

also from arbutin (see GLUCOSIDES), by boiling with dilute sulphuric acid, or by the action of emulsin:

$$C_{12}H_{16}O_7 + H_2O = C_6H_6O_2 + C_6H_{12}O_6.$$

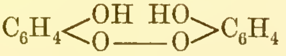
It is most easily prepared from quinone by reduction with sulphurous acid, $C_6H_4O_2 + H_2 = C_6H_6O_2$. Gaseous sulphur dioxide is passed into an aqueous solution of quinone, till the liquid, which at first assumes a brown colour from formation of quinhydrone, becomes colourless. The solution is then evaporated down, and the hydroquinone extracted by ether.

Hydroquinone crystallises from water in colourless rhombic prisms, melting at 169°, subliming when carefully heated, decomposing when suddenly heated. It dissolves in 17 parts of water at 15°, easily in alcohol and ether. It unites with hydrogen sulphide and sulphur dioxide, forming crystalline compounds which are decomposed by water. Its aqueous solution is turned red-brown by ammonia, and is not precipitated by lead-acetate except in presence of ammonia. Oxidising agents convert quinone first into quinhydrone, then into quinone:



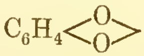
$$C_6H_4 < \substack{OH \\ OH}$$

Hydroquinone.



$$C_6H_4 < \substack{OH \quad HO \\ O \text{———} O} > C_6H_4$$

Quinhydrone.



$$C_6H_4 < \substack{O \\ O} >$$

Quinone.

Substitution-products of hydroquinone are obtained, not directly from hydroquinone, but from the corresponding derivatives of quinone or of arbutin.

Chlorhydroquinones are produced by reduction of chloroquinones with sulphurous acid. $C_6H_4Cl_2O_2$ melts at 158°, $C_5H_3Cl_3O_2$ at 134°, $C_6H_2Cl_4O_2$ above 200°.

Dinitrohydroquinone, $C_6H_4(NO_2)_2(OH)_2$, obtained by boiling dinitro-arbutin with dilute sulphuric acid, forms golden-yellow laminæ; its aqueous solution is coloured dark blue by alkalis.

Dichlorhydroquinone-disulphonic acid, $C_6Cl_2 \left\{ \begin{matrix} (OH)_2 \\ (SO_3H)_2 \end{matrix} \right.$, is formed by heating tetrachloroquinone with a dilute solution of acid sodium sulphite, tetrachlorhydroquinone being produced in the first instance, and two of its chlorine-atoms then replaced by the groups SO_3H. The aqueous solution of this acid is coloured indigo-blue by ferric chloride. A solution of its potassium salt, containing free potash, oxidises quickly on exposure to the air, and is converted into yellow potassium euthiochroate, $C_6(OH)_2 \left\{ \begin{matrix} O_2 \\ (SO_3K)_2 \end{matrix} \right.$.

Quinone, $C_6H_4 < \substack{O \\ O} >$, is produced by the oxidising action of manganese dioxide and sulphuric acid, or of dilute chromic acid, on numerous benzene-derivatives (*e.g.*, phenylenediamine, amidophenol, amidobenzene-sulphonic acid), especially those belonging to the para- series; also by distilling various vegetable extracts with MnO_2 and sulphuric acid. It is most easily prepared by gently heating quinic acid (1 part) with manganese dioxide (2 parts) and sulphuric acid (1 part diluted with ½ part water).

Quinone crystallises in golden-yellow prisms, melts at 116°, and sublimes, even at ordinary temperatures, in shining needles. It has a pungent tear-exciting odour, distils easily with aqueous vapour, and dissolves sparingly in cold water, easily in hot water, also in alcohol and ether. By reduction with sulphurous acid, or with zinc and hydrochloric acid, it is converted, first into quinhydrone, then into hydroquinone. Phosphorus pentachloride converts it into paradichlorobenzene.

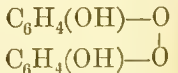
Chloroquinones are formed by the action of chlorine on quinone, and by distilling quinic acid with MnO_2 and hydrochloric acid. $C_6H_3ClO_2$, forms yellow needles. $C_6H_2Cl_2O_2$, produced also by the action of hypochlorous anhydride, Cl_2O, on benzene, and by heating trichlorophenol with nitric acid, forms large yellow prisms, melting at 120°. $C_6HCl_3O_2$, obtained also by the action of chromyl chloride, CrO_2Cl_2, on benzene, crystallises in large laminæ melting at 166°.

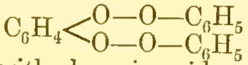
Tetrachloroquinone or *Chloranil*, $C_6Cl_4O_2$, is formed, together with $C_6HCl_3O_2$, from many benzene-derivatives (aniline, phenol, isatin, &c.) by the action of chlorine, or of potassium chlorate and hydrochloric acid. It is best prepared by gradually adding a mixture of 1 part crystallised phenol, and 4 parts potassium chlorate to hydrochloric acid diluted with an equal volume of water, and slowly heating the liquid. Red crystals then separate, which, on further addition of potassium chlorate, are converted into a yellow mixture of tri- and tetra-chloroquinone. To separate these compounds, they are converted by sulphurous acid into the corresponding chlorohydroquinones ($C_6H_2Cl_4O_4$ is insoluble in water), which are then reconverted into the chloroquinones by oxidation.

Chloranil forms golden-yellow shining laminæ, insoluble in water, soluble in hot alcohol and in ether, subliming at about 150°; converted by PCl_5 into perchlorobenzene.

Chloranil dissolves with purple-red colour in dilute potash-ley, forming the potassium salt of chloranilic acid; $C_6Cl_2O_2(OK)_2 + H_2O$, which crystallises in dark red needles, sparingly soluble in water. Acids decompose it, separating chloranilic acid, $C_6Cl_2O_2(OH)_2 + H_2O$, in reddish shining scales. Chloranil is converted by aqueous ammonia into chloranilamide, $C_6Cl_2O_2(NH_2)_2$, and chloranilamic acid, $C_6Cl_2(NH_2)O_2(OH)$.

Bromoquinones, analogous to the chloroquinones, are obtained by similar reactions. *Bromanil*, $C_6Br_4O_2$, is most readily prepared by heating phenol (1 part) with bromine (10 parts), iodine (3 parts), and water, to 100°. Golden-yellow laminæ sparingly soluble in carbon sulphide.

Quinhydrone, $C_{12}H_{10}O_4 = C_6H_6O_2.C_6H_4O_2 =$  $\begin{matrix} C_6H_4(OH){-}O \\ | \\ C_6H_4(OH){-}O \end{matrix}$, is formed by treating quinone in aqueous solution with a quantity of sulphurous acid not sufficient for complete reduction; also by incomplete oxidation of hydroquinone, and by mixing the aqueous solutions of quinone and hydroquinone. It crystallises in flat prisms, having a splendid golden-green metallic lustre like that of the wing-cases of the rose-beetle, and sublimes in green laminæ. It is fusible, has but little odour, dissolves freely in hot water with a brown colour, in alcohol and ether with green colour. It is resolved, by boiling with water, into quinone which distils over, and hydroquinone; and is converted, by oxidation into quinone, by reduction into hydroquinone.

Phenoquinone,  $C_6H_4<\begin{matrix}O—O—C_6H_5\\O—O—C_6H_5\end{matrix}$, is produced by careful oxidation of phenol with chromic acid, and (together with quinhydrone and hydroquinone) by mixing the aqueous solutions of quinone and phenol. It forms red, very volatile needles, melting at 71°, soluble in water, more easily in alcohol and ether. It is coloured blue by potash, green by baryta or ammonia.

Diatomic Phenols, $C_7H_8O_2 = C_6H_3(CH_3)(OH)_2$. — *Orcin* exists ready formed in all the lichens (*Lecanora tartarea, Rocella tinctoria, Variolaria orcina,* &c.) which are used for the preparation of archil and litmus; and is the general product of the decomposition of certain acids extracted from these lichens (orsellinic acid, erythric acid, &c.) under the influence of heat or of alkalis. Orsellinic acid, $C_8H_8O_4$, when boiled with baryta-water, splits up into carbon dioxide and orcin:

$$C_8H_8O_4 = CO_2 + C_7H_8O_2.$$

Evernic acid is resolved by the same treatment into everninic and orsellinic acids:

$$\underset{\text{Evernic.}}{C_{18}H_{16}O_7} + H_2O = \underset{\text{Everninic}}{C_9H_{10}O_4} + \underset{\text{Orsellinic.}}{C_3H_8O_4}.$$

Erythric acid (erythrin) is resolved in like manner into orsellinic acid and picroerythrin:

$$\underset{\text{Erythrin.}}{C_{20}H_{22}O_{10}} + H_2O = \underset{\substack{\text{Orsellinic}\\\text{acid.}}}{C_8H_8O_4} + \underset{\text{Picroerythrin}}{C_{12}H_{16}O_7},$$

the orsellinic acid being further resolved as above into CO_2 and orcin, and the pycroerythrin into CO_2, erythrite (p. 186), and orcin:

$$C_{12}H_{16}O_7 + H_2O = CO_2 + C_4H_{10}O_4 + C_7H_8O_2.$$

To prepare orcin in quantity, one of the lichens above mentioned is boiled with milk of lime, the liquid filtered and evaporated to one-fourth; the lime precipitated by carbonic acid; the filtrate evaporated nearly to dryness on the water-bath; the residue boiled several times with benzene; the orcin extracted from the benzene-solution by agitation with water; and the aqueous solution evaporated.

Orcin may also be prepared by the action of melting potash on extract of aloes, and on the potassium-salt of chlorotoluene-sulphonic acid.

Orcin crystallises in colourless six-sided prisms containing $C_7H_8O_2.H_2O$. It has a sweet taste; dissolves readily in water, alcohol, and ether; melts at 58°; gives off its water of crystallisation at 86°, and boils at 290°. Its aqueous solution is precipitated by lead acetate, coloured blue-violet by ferric chloride, and exhibits with hypochlorites a transient dark violet coloration.

The hydroxyl-groups in orcin may be replaced by acid and by alcoholic radicles; the diethylic ether, $C_7H_6(OC_2H_5)_2O_2$, boils at 240°–250°.

Tribromorcin, $C_6Br_3(CH_3)(OH)_2$, is precipitated by bromine-water from the aqueous solution of orcin.

Trinitro-orcin, $C(NO_2)_3(CH)_3(OH)_2$, produced by dissolving orcin in a well-cooled mixture of strong nitric and sulphuric acid, forms long yellow needles, which melt at 162°, and react very much like trinitroresorcin. By the action of tin and hydrochloric acid it is reduced to *triamido-orcin*, $C_6(NH_2)_3(CH_3)(OH)_2$, which forms colourless crystals, and is converted by exposure to the air into crystals of *amido-dimido-orcin*, $C_6(CH)_3NH_2{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}$.

Orcin unites with dry *ammonia*, forming a crystalline compound, $C_7H_8O_2.NH_3$; and when a solution of orcin containing ammonia is exposed to the air, it absorbs oxygen, acquires a dark red or purple colour, and gives with acetic acid a deep red pulverulent precipitate of orcein, $C_7H_7NO_3$, formed according to the equation:

$$C_7H_8O_2 + NH_3 + O_3 = C_7H_7NO_3 + 2H_2O .$$

Orcein unites with metallic oxides, forming red lakes. It is the chief constituent of the dye-stuffs known as archil, cudbear, French purple, and litmus. The last-mentioned substance, which is extensively used for the preparation of test-papers, is prepared from *Roccella tinctoria* or *Lecanora tartarca*, by macerating the lichen in solution of ammonium carbonate, exposing the liquid to the air for 20 to 40 days, and thickening the colouring matter thus obtained with chalk or gypsum.

Isorcin, $C_6H_3(CH_3)(OH)_2$, obtained from toluidine-disulphonic acid, forms colourless needles, melts at 87°, and boils at 260°.

Homopyrocatechin, $C_7H_8O_2 = C_6H_3(CH_3)(OH)_2$, which has not been obtained in the crystalline state, is produced by the action of hydriodic acid on creasol, $C_8H_{10}O_2 = C_7H_6{<}\begin{smallmatrix}OH\\OCH_3\end{smallmatrix}$, which is its methylic ether. Creasol is one of the constituents of beech-tar (p. 489), and is formed together with guaiacol, by the dry distillation of guaiac resin. It is a colourless liquid, very much like guaiacol, boils at 219°, and reduces silver nitrate when heated with it. Its alcoholic solution is coloured dark green by ferric chloride.

Hydrotoluquinone, $C_6H_3(CH_3)(OH)_2$, and *Toluquinone*, $C_6H_3(CH_3)O_2$, are not known; but di- and tri-chlorotoluquinone, $C_6HCl_2(CH_3)O_2$ and $C_6Cl_3(CH_3)(OH)_2$, are formed by the action of hydrochloric acid and potassium chlorate on cresol, just as the six-carbon chloroquinones are obtained from phenol. The trichloro-compound forms yellow laminar crystals, and is converted by heating with aqueous sulphurous acid into trichloro-hydrotoluquinone, $C_6Cl_3(CH_3)(OH)_2$, which crystallises in colourless needles.

Diatomic Phenols, $C_8H_{10}O_2 = C_8H_8(OH)_2$. — Hydrophlorone is obtained by the action of sulphurous acid on phlorone, or xyloquinone, $C_8H_8O_2$,—a compound obtained by distilling coal-tar oil or beech-tar creosote, boiling above 210° with MnO_2 and sulphuric acid. It forms colourless laminæ, having a mother-of-pearl lustre, fusible, sublimable, easily soluble in water, alcohol, and ether. Oxidising agents convert it into phlorone, $C_8H_8O_2$, which forms yellow volatile needles.

Beta-orcin is obtained by dry distillation of usnic acid and other acids occurring in lichens, *e.g.*, $C_9H_{10}O_4$ (evernic acid) $= C_8H_{10}O_2 + CO_2$. Colourless crystals, easily soluble in hot water, melting at 109°. The aqueous solution turns red when mixed with ammonia and exposed to the air, and is coloured dark red by bleaching powder.

Veratrol, obtained by distillation of veratric acid, $C_8H_{10}O_4$, with baryta, is an oil solidifying at $+15°$, and boiling at 202°–205°.

Thymohydroquinone, $C_{10}H_{12}(OH)_2 = C_6H_2(CH_3)(C_3H_7)(OH)_2$, the only known diatomic phenol containing 10 atoms of carbon, is produced by the action of sulphurous acid on thymoquinone, and crystallises in limpid, shining, four-sided prisms, melting at 139·5°, and subliming without decomposition; converted by oxidation into thymoquinone. Its methylic ether is a constituent of the volatile oil of *Arnica montana.*

Thymoquinone, $C_{10}H_{12}{<}\begin{matrix}O\\O\end{matrix}{>}$ (*thymoïl*), is produced by distilling thymol and carvacrol with MnO_2 and sulphuric acid. It crystallises in yellow tables, melts at 45·5°, and boils at 200°.

Triatomic Phenols, $C_6H_3(OH)_3$.

Pyrogallol or **Pyrogallic Acid**, is produced by the action of heat on gallic (dioxysalicylic) acid: $C_7H_6O_5 = CO_2 + C_6H_6O_3$; also, together with gallic acid, by the action of hot caustic potash on di-iodosalicylic acid, $C_7H_4I_2O_3$. It is conveniently prepared by heating a dried aqueous extract of gall-nuts to 180°–185° in an iron pot covered with a paper cap; it then sublimes and condenses on the cap in long flattened prisms.

Pyrogallol is soluble in water, alcohol, and ether; it melts at 115°, boils at 210°, and decomposes at 250°, giving off water, and leaving a residue of metagallic acid, $C_6H_4O_2$. Pyrogallol dissolves in caustic potash or soda, forming a solution which quickly absorbs oxygen from the air, and turns black; this solution forms a very convenient reagent for the eudiometric analysis of air (i. 154). With solutions of ferrous salts, it produces a black-blue colour; with ferric salts a red colour. Pyrogallol quickly reduces gold, silver, and mercury from their salts, and forms, with lead acetate, a white precipitate, $C_6H_6O_3PbO$.

With *bromine* pyrogallol forms a tribromo-derivative, $C_6Br_3(OH_3)$; with *acetyl chloride* it yields a triacetyl-derivative, $C_6H_3(OC_2H_3O)_3$, forming crystals slightly soluble in water.

Phloroglucin, $C_6H_6O_3$.—Phlorizin, or Phloridzin, $C_{21}H_{24}O_{10}$, a crystalline substance found in the root-bark of the apple, pear, plum, and cherry trees, is resolved by boiling with dilute acids into glucose and phloretin, $C_{15}H_{14}O_5$:

$$C_{21}H_{24}O_{10} + H_2O = C_6H_{12}O_6 + C_{15}H_{14}O_5 ;$$

and phloretin heated with aqueous potash is resolved into phloretic acid and phloroglucin :

$$C_{15}H_{14}O_5 + H_2O = C_9H_{10}O_3 + C_6H_6O_3 .$$

Phloroglucin crystallises in large colourless prisms containing $2H_2O$; effloresces on exposure to the air; gives off all its crystallisation-water at 100°; melts at 230°, and sublimes without decomposition. It has a sweet taste, and dissolves easily in water, alcohol, and ether. Its aqueous solution is precipitated by lead acetate, and coloured dark violet by ferric chloride.

Phoroglucin is converted by chlorine into dichloracetic acid; with *bromine* and with nitric acid it forms tri-substitution derivatives; with *acetyl chloride* and *benzoyl chloride* it yields the ethers $C_6H_3\left\{\begin{matrix}(OH)_2\\OC_2H_3O\end{matrix}\right.$ and $C_6H_3\left\{\begin{matrix}(OH)_2\\OC_7H_5O\end{matrix}\right.$, both of which are crystalline. Its dibutyryl-ether, $C_6H_3\left\{\begin{matrix}OH\\(OC_4H_7O)_2\end{matrix}\right.$, called *filicic acid*, occurs in the root of the male fern (*Aspidium Filix mas*) as a crystalline substance, which is resolved by fusion with potash into phloroglucin and butyric acid.

With *ammonia* phloroglucin forms the basic compound, phloramine, $C_6H_3\left\{\begin{matrix}(OH)_2\\NH_2\end{matrix}\right.$, which forms crystalline salts with acids.

Appendix to the Phenols.—PHENOL-DYES.

Aurin or Rosolic Acid, $C_{20}H_{14}O_3$ (or $C_{20}H_{16}O_3$?)—This compound, also called *Corallin*, is a red colouring matter, obtained by heating phenol with oxalic and sulphuric acid, the oxalic acid being then resolved into CO, CO_2, and H_2O, and the CO reacting with the phenol, as shown by the equation :

$$3C_0H_0O + 2CO = C_{20}H_{14}O_3 + 2H_2O .$$

To obtain a pure product, the mixture of sulphuric acid and phenol must be heated on a water-bath, and the oxalic acid added gradually, waiting each time till the evolution of gas ceases, and not using sufficient oxalic acid to attack all the phenol. The aurin thus obtained has exactly the composition $C_{20}H_{14}O_3$.*

A commercial dye-stuff, known as aurin, corallin, or pæonin, which gives a fine yellow-red colour to wool and silk, is prepared in a similar manner. It is a mixture of several substances, but may be purified by treatment with aqueous ammonia, which dissolves the extraneous matters, leaving a residue of nearly pure aurin.

The same compound is obtained by the action of nitrous acid on rosaniline (p. 462); and it is reconverted into that base by heating with ammonia in aqueous or alcoholic solution:

$$C_{20}H_{14}O_3 + 3NH_3 = C_{20}H_{17}N_3 + 3H_2O.$$

From this it would appear that the formula of rosaniline should be $C_{20}H_{17}N_3$, whereas, according to Hofmann's analysis, its composition is $C_{20}H_{19}N_3$. Further investigation is therefore required to clear up this discrepancy.†

Aurin crystallises from alcohol in red prisms, having a green metallic lustre. It is insoluble in water, but soluble in alcohol, strong hydrochloric acid, and glacial acetic acid. It unites with sulphurous anhydride, forming garnet-red crystals, $(C_{20}H_{14}O_3)_2SO_2 + 5\frac{1}{2}H_2O$, and forms crystalline compounds with bisulphites of alkali-metal, *e.g.*, $C_{20}H_{14}O_3.NaHSO_3$. Bromine added to its acetic acid solution throws down the compound $C_{20}H_{10}Br_4O_3$ in shining green laminæ.

By reduction with zinc-dust in alcoholic solution, aurin is converted into leucaurin, $C_{20}H_{10}O_3$, which crystallises from alcohol in colourless prisms, and is reconverted into aurin by oxidation. *Triacetyl-leucaurin*, $C_{20}H_{13}(C_2H_3O)_3O_3$, produced by heating leucaurin with acetyl chloride, forms short silky needles, easily soluble in alcohol and in acetic acid.

Phthaleins.—These are compounds formed, with elimination of water, by the combination of phenols with phthalic anhydride, $C_8H_4O_3$ or $C_6H_4{<}\substack{CO\\CO}{>}O$. They contain the ketonic group CO, together with the hydroxyl-groups of the phenols, and are consequently intermediate in character between the phenols and ketones. They are all more or less coloured, and act as dyestuffs. By hydrogenation (action of zinc-dust in alkaline solution) they are converted into phthalins, colourless compounds in which the ketonic groups are converted into alcoholic groups, C(OH); *e.g.*,

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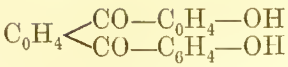
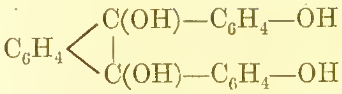
* Dale and Schorlemmer, Chem. Soc. Jour. 1873, 434; and 1877, vol. ii. p. 121.

† Dale and Schorlemmer observe that, in the analysis of organic colouring matters, the percentage of hydrogen is often found too high.



$$C_6H_4\left<\begin{array}{l}CO-C_6H_4-OH\\CO-C_6H_4-OH\end{array}\right.$$

Phenol-phthalein.

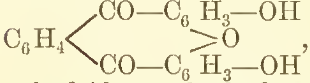


$$C_6H_4\left<\begin{array}{l}C(OH)-C_6H_4-OH\\ |\\ C(OH)-C_6H_4-OH\end{array}\right.$$

Phenol-phthalin.

By oxidation, the phthalins are reconverted into phthaleins.

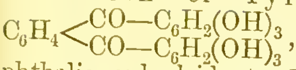
Phenol-phthalein, $C_{20}H_{14}O_4$, is prepared by heating 10 parts of phenol with 5 parts of phthalic anhydride and 4 parts of strong sulphuric acid to 120° for about ten hours, exhausting the product with boiling water, dissolving the residue in dilute caustic soda, and precipitating with acetic acid and a little hydrochloric acid. It may be prepared by boiling its alcoholic solution with animal charcoal, and precipitating the filtrate with water. It then separates as a white or yellowish-white crystalline powder, or in triclinic crystals, according as the precipitation is effected quickly or slowly. It dissolves in alkalis with fuchsine-red colour, and on heating the alkaline solution with zinc-dust, it becomes colourless, from conversion of the phthalein into phenol-phthalin, $C_{20}H_{16}O_4$, which separates on addition of hydrochloric acid, in white prisms. This compound dissolves in strong sulphuric acid, and the solution, mixed with water, deposits an amorphous yellowish substance, $C_{20}H_{14}O_3$, called phenol-phthalidin, which may be reconverted into the phthalin by heating with water to 175°. By exposure to the air, or more quickly, by treatment with manganese dioxide, potassium manganate, or potassium ferricyanide, it is converted into a compound, $C_{20}H_{14}O_4$, isomeric with phenol-phthalein, which separates in monoclinic crystals.



Resorcin-phthalein or Fluorescein, $C_{20}H_{12}O_5$ = $C_6H_4\left<\begin{array}{l}CO-C_6H_3-OH\\ \qquad\qquad >O\\ CO-C_6H_3-OH\end{array}\right.$, prepared by heating resorcin with phthalic anhydride to 200°, forms dark-brown crystals, which dissolve in ammonia, forming a red solution with splendid green fluorescence. On adding bromine to its solution in glacial acetic acid, tetrabromoresorcin-phthalein, or Eosin, gradually separates in crystals, which may be purified by conversion into a potassium salt and precipitation with an acid. From dilute alcohol it separates in dull, flesh-coloured crystals; from absolute alcohol in red crystals containing 1 molecule of alcohol. Its potassium salt, $C_{20}H_6Br_4O_5K_2$, known in commerce as "soluble eosin," dyes silk of a fine rose-colour.

Pyrocatechin-phthalein, $C_{20}H_{12}O_5$, formed by gently heating pyrocatechin with phthalic anhydride and sulphuric acid, dissolves in potash-ley with a fine blue colour. Hydroquinone-phthalein, formed in like manner, dissolves in strong sulphuric acid with brick-red colour, in alkalis with violet colour.

Orcin-phthalein, $C_{22}H_{10}O_5$, forms colourless needles, dissolving in alkalis with dark-red colour, without fluorescence.

Gallein or Pyrogallol-phthalein, $C_{20}H_{14}O_8$ =  $C_6H_4<\begin{matrix}CO-C_6H_2(OH)_3\\CO-C_6H_2(OH)_3\end{matrix}$, produced by heating pyrogallol with phthalic anhydride to 190°–200°, forms a brown-red powder or small crystals, with green surface-colour. It dissolves in alcohol with dark-red, in potash-ley with fine blue colour. By zinc-dust, or by zinc and sulphuric acid, it is converted into gallin, $C_{20}H_{18}O_7$, which forms nearly colourless crystals, and is converted by heating to 200°, with strong sulphuric acid, into cœrulein, $C_{20}H_{10}O_7$, a blue dye-stuff which dissolves in alkalis with green, in aniline with splendid blue colour, and is reduced by zinc-dust to cœrulin.

Normal Aromatic Alcohols.

These compounds, formed by substitution of OH for H in the lateral chains of the hydrocarbons homologous with benzene, contain the group CH_2OH, and are therefore primary alcohols, convertible by oxidation into aldehydes and acids containing the same number of carbon-atoms as the alcohols themselves, and producible by methods similar to those which yield the primary alcohols of the fatty series, viz. (1.) From the hydrocarbons by conversion, first into haloïd derivatives, such as $C_6H_5.CH_2Cl$, then into acetic ethers, and saponification of the latter with caustic alkalis; *e.g.*,

$$\underset{\text{Benzyl acetate.}}{C_6H_5.CH_2.OC_2H_3O} + KOH = C_2H_3O.OK + \underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2.OH}\,.$$

(2.) From the aldehydes, by the action of nascent hydrogen, or by heating with alcoholic potash:

$$\underset{\text{Benzaldehyde.}}{2(C_6H_5.CHO)} + KOH = \underset{\substack{\text{Benzyl}\\\text{alcohol.}}}{C_6H_5.CH_2.OH} + \underset{\substack{\text{Potassium}\\\text{benzoate.}}}{C_6H_5.CO_2K}\,.$$

Monatomic Alcohols.

Benzyl Alcohol, $C_7H_8O = C_6H_5.CH_2OH$, may be prepared by the methods just mentioned, or by the action of nascent hydrogen on benzoic or hippuric acid. Its benzoic ether, $C_7H_5O_2.C_7H_7$, is one of the constituents of Peru and Tolu balsams.

Benzyl alcohol is a colourless, strongly refracting, oily liquid, having a specific gravity of 1·051 at 14°, and boiling at 207°. It is insoluble in water, but soluble in all proportions in common alcohol, ether, acetic acid, and carbon bisulphide. By oxygen in presence of platinum black, or by nitric acid, it is converted into benzoic aldehyde; by aqueous chromic acid, into benzoic acid:

$$C_6H_5.CH_2OH + O = H_2O + C_6H_5.CHO\,,$$

and

$$C_6H_5.CH_2OH + O_2 = H_2O + C_6H_5.CO(OH)\,.$$

Strong hydrochloric acid converts it into benzyl chloride, C_7H_7Cl. Distilled with acetic acid and strong sulphuric acid, it is converted into benzyl acetate, $C_7H_7(OC_2H_3O)$, a liquid having an odour of pears, and boiling at 210°. Benzyl oxalate, $C_2O_4(C_7H_7)_2$, forms shining laminæ melting at 80°.

Alcoholic benzyl ethers are formed by heating benzyl chloride with solutions of potash in the corresponding alcohols. Methyl benzylate, $C_7H_7.O.CH_3$, boils at 168°; ethyl benzylate, $C_7H_7.O.C_2H_5$, at 185°. Benzyl-phenylate, $C_7H_7.O.C_6H_5$, formed by heating benzyl chloride with potassium phenate, $C_6H_5.OK$, melts at 39°, and boils at 287°. Dibenzyl ether, $(C_7H_7)_2O$, obtained by heating benzyl alcohol with boric oxide, $[2C_7H_7(OH) - H_2O = (C_7H_7)_2O]$, or by heating benzyl chloride with water to 190°, is an oil boiling above 300°.

Chlorobenzyl alcohol (para), $C_7H_4Cl.CH_2OH$, produced by heating parachlorobenzyl chloride, $C_6H_4Cl.CH_2Cl$, with aqueous ammonia, forms long needles, melts at 66°, and boils without decomposition. Other haloïd benzyl alcohols are formed in a similar manner.

Paranitrobenzyl alcohol, $C_6H_4(NO_2).CH_2OH$, produced by saponification of paranitrobenzyl acetate (obtained by nitration of benzyl acetate), is soluble in hot water, and melts at 93°.

Benzyl hydrosulphide or Benzyl mercaptan, $C_6H_5.CH_2SH$, obtained by the action of alcoholic potassium hydrosulphide on benzyl chloride, is a liquid having an alliaceous odour, a specific gravity of 1·058 at 20°, and boiling at 194°. Its alcoholic solution gives, with metallic salts, precipitates consisting of benzyl-mercaptides, *e.g.* $(C_6H_5.CH_2S)_2Hg$.

Benzyl sulphide, $(C_6H_5.CH_2)_2S$, formed by the action of potassium monosulphide on benzyl chloride, in alcoholic solution, crystallises in colourless needles melting at 49°. By oxidation with nitric acid, it is converted into benzyl oxysulphide, $(C_6H_5.CH_2)_2SO$, which is soluble in hot water, and melts at 130°.

Benzyl disulphide, $(C_6H_5.CH_2)_2S_2$, formed by oxidation of benzyl mercaptan exposed to the air, crystallises from alcohol in shining scales melting at 66°. Nascent hydrogen converts it into benzyl mercaptan.

All these sulphur-compounds of benzyl are decomposed by heat.

Xylyl Alcohol,* $C_8H_{10}O = C_6H_4{<}\begin{smallmatrix}CH_3\\CH_2OH\end{smallmatrix}$.—Of the three isomeric modifications of this alcohol only the para-compound is known. It is obtained from the corresponding aldehyde, and from paraxylyl chloride, $C_6H_4(CH_3).CH_2Cl$, by the methods above described. It crystallises in needles, dissolves sparingly in water, melts at 59°, and boils at 217°. Nitric acid converts it into toluic aldehyde, $C_6H_4(CH_3).CHO$. By heating with hydrochloric acid it is reconverted into xylyl chloride. Its acetic ether boils at 243°. The chloride treated with KHS and K_2S yields the compounds $C_8H_9(SH)$ and $(C_8H_9)_2S$.

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* Generally called tolyl alcohol; but this name is inappropriate. If $C_6H_4(CH_3).CH_2OH$ is to be called *tolyl alcohol*, then $C_6H_5.CH_2OH$ should by analogy be called, not benzyl alcohol, but *phenyl alcohol*. The true tolyl alcohol is cresol, $C_6H_4{<}\begin{smallmatrix}CH_3\\OH\end{smallmatrix}$, metameric with benzyl alcohol, $CH_2{<}\begin{smallmatrix}C_6H_5\\OH\end{smallmatrix}$.

Metameric with the xylyl alcohols are—(1.) Primary phenyl-ethyl alcohol, $C_6H_5.CH_2.CH_2.OH$, formed by the action of sodium amalgam on a solution of alpha-toluic (phenyl-acetic) aldehyde, $C_6H_5.CH_2.CHO$, dissolved in aqueous alcohol. Colourless liquid, boiling at 212°. Specific gravity, 1·0337 at 21°. Converted by gradual oxidation into alpha-toluic acid. Its acetic ether boils at 224°.

(2.) Secondary phenyl-ethyl alcohol, $C_6H_5.CHOH.CH_3$, prepared from bromethyl-benzene, $C_6H_5.CHBr.CH_3$ (p. 441), in the same manner as benzyl alcohol from benzyl chloride; and by the action of sodium-amalgam on acetophenone, $C_6H_5.CO.CH_3$. It is a colourless liquid, boiling at 202°–203°, having a density of 1·013, and reconverted by oxidation into acetophenone.

Phenyl-propyl Alcohol, $C_9H_{12}O=C_6H_5.CH_2.CH_2.CH_2.OH$, produced by the action of nascent hydrogen on styryl alcohol or cinnamic alcohol, $C_9H_{14}O$, is a liquid boiling at 235°.—Secondary phenyl-propyl alcohol, $C_6H_5.CH_2.CH(OH).CH_3$, formed by the action of nascent hydrogen on ethyl-phenyl ketone, is a liquid boiling at 210°–211°.

Cymyl Alcohol, $C_{10}H_{14}O=C_{10}H_{13}(OH)=C_9H_{11}.CH_2OH$, also called *Cumylic Alcohol.*—This alcohol, discovered by Kraut, is produced, together with cumic acid, $C_{10}H_{12}O_2$, by the action of alcoholic potash on cumic aldehyde:

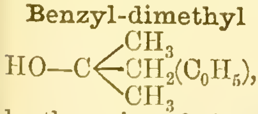
$$2C_{10}H_{12}O + KOH = C_{10}H_{11}KO_2 + C_{10}H_{14}O.$$

It is a colourless liquid, boiling at 243°, insoluble in water, soluble in all proportions in common alcohol and ether. Nitric acid converts it into cumic acid. Boiled with alcoholic potash, it is converted into potassium cumate and cymene:

$$3C_{10}H_{14}O + KOH = C_{10}H_{11}KO_2 + 2C_{10}H_{14} + 2H_2O.$$

Hydrochloric acid gas converts it into cymyl chloride, $C_{10}H_{13}Cl$ Metameric with this compound is:

Benzyl-dimethyl Carbinol, or Phenyl-katabutyl Alcohol,



$$HO-C\begin{cases}CH_3\\CH_2(C_6H_5)\\CH_3\end{cases}$$

obtained, similarly to tertiary butyl alcohol, by the action of zinc-methyl on phenyl-acetic or α-toluic chloride, $C_6H_5.CH_2.COCl$. It crystallises in long colourless needles, melts at 20°–22°, and boils at 220°–230°.

Sycoceryl Alcohol, $C_{18}H_{30}O = C_{18}H_{29}(OH) = C_{17}H_{27}.CH_2OH$, —This compound, discovered by De La Rue and Müller, is produced by the action of alcoholic soda on sycoceryl acetate (a crystalline substance extracted from the resin of *Ficus rubiginosa*), and purified by precipitation with water or by crystallisation from common alcohol. It forms very thin crystals resembling caffeine, and melting at 90° to a liquid heavier than water. It is slowly attacked by dilute nitric acid, yielding a crystalline mass apparently consisting of a mixture of sycoceric acid, $C_{18}H_{28}O_2$, and nitrosycoceric acid, $C_{18}H_{27}(NO_2)O_2$. Boiled with dilute aqueous chromic acid, it yields thin prisms, probably of sycoceric aldehyde, $C_{18}H_{28}O$. With acetyl chloride, it forms crystalline sycoceryl acetate:

$$C_{18}H_{29}OH + C_2H_3OCl = HCl + C_{18}H_{29}.O.C_2H_3O\,.$$

With benzoic acid it yields, in like manner, sycoceryl benzoate, $C_{18}H_{29}.O.C_7H_5O$, which crystallises in prisms from solution in benzene or chloroform.

The resin of *Ficus rubiginosa*, an Australian plant, is resolved by treatment with alcohol, into about 73 per cent. of sycoretin, soluble in cold alcohol, 14 per cent. of syoceryl acetate, soluble in hot alcohol, and 13 per cent. of residue, consisting of caoutchouc, sand, and fragments of bark. Sycoretin is an amorphous white neutral resin, very brittle, and highly electric; it melts in boiling water to a thick liquid which floats on the surface. It dissolves easily in alcohol, ether, chloroform, and oil of turpentine.

Diatomic Alcohols.

Benzylene Glycol, $C_6H_5.CH(OH)_2$, appears (for reasons already assigned, p. 167), to be incapable of existing, the reactions which might be expected to produce it leading in reality to the production of benzaldehyde, $C_6H_5.CHO$. Its ethers are formed from benzal chloride, $C_6H_5.CHCl_2$ (p. 439), by the action of sodium alcoholates, or of the salts of organic acids. The *dimethylic ether*, $C_6H_5.CH(OCH_3)_2$, boils at 208°; the *diethylic ether*, $C_6H_5.CH(OC_2H_5)_2$ at 222°. The *acetic ether*, $C_6H_5.CH(O.C_2H_3O)_2$, is crystalline; melts at 36°, and boils at 190°, being resolved at the same time into benzaldehyde and acetic anhydride.

Xylylene Glycol (para), $C_6H_4{<}\begin{matrix}CH_2.OH\\CH_2.OH\end{matrix}$, obtained by heating paraxylylene bromide or dibromoparaxylene, $C_6H_4(CH_2Br)_2$, with water to 170°–180°, crystallises in colourless needles melting at 112°–113°, easily soluble in water, converted by oxidising agents into terephthalic acid. Its diacetic ether, $C_6H_4(CH_2.OC_2H_3O)_2$, melts at 47°.

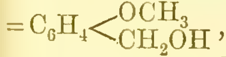
The following compounds have the hydroxyl groups, partly in the principal, partly in the lateral chains, and are therefore both alcohols and phenols.

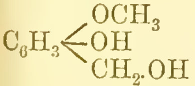
Saligenin, $C_7H_8O_2 = C_6H_4(OH)\text{—}CH_2OH$, or *Ortho-oxybenzyl alcohol,* is formed by the action of nascent hydrogen on salicylic aldehyde, $C_6H_4(OH).CHO$; and by decomposition of salicin, $C_{13}H_{18}O_7$ (a bitter substance found in willow and poplar bark), under the influence of emulsin or synaptase, the ferment of sweet almonds :

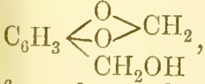
$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Saligenin.}}{C_7H_8O_2}.$$

Saligenin forms colourless, nacreous scales, freely soluble in water, alcohol, and ether. It melts at 82°, and decomposes at about 100°. Dilute acids at boiling heat convert it into saliretin, C_7H_6O, a resinous substance differing from saligenin by the elements of water. The same substance is produced directly from salicin by boiling with dilute acids. Many oxidising agents, as chromic acid and silver oxide, convert saligenin into salicylic aldehyde and salicylic acid : this shows that it is an ortho-compound. The aqueous solution of saligenin gives a deep indigo-blue colour with ferric salts.

Chlorinated derivatives of saligenin, viz., $C_7H_7ClO_2$ and $C_7H_6Cl_2O_2$, are obtained by the action of synaptase on the corresponding chlorosalicin.

Anisyl Alcohol or **Methyl-paraoxybenzyl Alcohol,** $C_8H_{10}O_2$  $= C_6H_4{<}{\begin{smallmatrix}OCH_3\\CH_2OH\end{smallmatrix}}$, is prepared from anisaldehyde (p. 512), in the same manner as benzyl alcohol from benzaldehyde. It crystallises in colourless shining prisms; has a faint odour and burning taste; melts at 25°, and distils undecomposed at 258·8°. By oxidising agents it is converted into anisaldehyde and anisic acid; by hydrochloric acid into a volatile chloride, $C_6H_4(OCH_3).CH_2Cl$.

Vanillic or **Methyl-protocatechuic Alcohol,** $C_8H_{10}O_3 =$  $C_6H_3{<}{\begin{smallmatrix}OCH_3\\OH\\CH_2.OH\end{smallmatrix}}$, obtained by the action of sodium-amalgam on an aqueous solution of vanillin (*q. v.*), forms colourless prismatic crystals, melting at 103°–105°, soluble in water and in alcohol.

Piperonylic or **Methene-protocatechuic Alcohol,** $C_8H_8O_3 =$  $C_6H_3{<}{\begin{smallmatrix}O\\O\\CH_2OH\end{smallmatrix}}$ with $\begin{smallmatrix}O\\O\end{smallmatrix}{>}CH_2$, obtained in like manner from piperonal (*q. v.*), forms long colourless prisms, melting at 57°, sparingly soluble in cold, more easily in hot water, very soluble in alcohol.

A triatomic alcohol called **Stycerin** or **Phenyl-glycerin,** $C_9H_{12}O_3 = C_6H_5.CH(OH).CH(OH).CH_2OH$, formed by heating the corresponding dibromhydrin, $C_6H_5.CHBr.CHBr.CH_2OH$, with water to 100° for 24 hours, is a light yellow gummy mass, easily soluble in water and in alcohol. The *dibromhydrin,* obtained by direct combination of bromine with styryl alcohol, forms large colourless shining plates or slender needles, melting at 74°. The tribromhydrin, $C_9H_9Br_3 = C_6H_5.CHBr.CHBr.CH_2Br$, obtained by treating the dibromhydrin with excess of concentrated hydrobromic acid, forms shining needles melting at 124°.

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2. Unsaturated Alcohols and Phenols :

Cinnyl Alcohol, Styryl Alcohol, or **Styrone,** $C_9H_{10}O$, $= C_9H_9OH$, or $C_6H_5CH{=}CH.CH_2OH$, is obtained by heating styracin or cinnyl cinnamate, $C_9H_9(OC_9H_7O)$, (a compound contained in liquid storax and in balsam of Peru), with caustic alkalis. It crystallises in soft silky needles, having a sweet taste and an odour of hyacinths, melting at 33°, and volatilising, without decomposition, at a higher temperature. It is moderately soluble in water, freely in alcohol and ether. By oxidising agents it is converted into cinnamic aldehyde, C_9H_8O, and cinnamic acid, $C_4H_8O_2$, being related to those compounds in the same manner as ethyl alcohol to acetic aldehyde and acetic acid. With *fuming sulphuric acid* it forms a sulpho-acid, $C_9H_{10}SO_3$, the barium-salt of which is soluble in water. It unites directly with 2 atoms of bromine, forming styceric dibromhydrin, $C_9H_{10}Br_2O$ (p. 505).

Allyl-phenol or **Anol**, $C_9H_{10}O = C_6H_4(OH)(C_3H_5)$, formed by fusing anisaldehyde (p. 512) with potash, crystallises in shining laminæ, melting at 92°, and decomposing when distilled.

Methyl-allyl Phenol, Anethol or **Anise-Camphor,** $C_{10}H_{12}O = C_6H_4(OCH_3)(C_3H_5)$, is a constituent of the volatile oils of anise, fennel and tarragon, and separates therefrom on cooling in soft shining scales, melting at 20°, and boiling at 225°. By oxidation with chromic acid, it is resolved into acetic and anisic acids. On heating it with hydriodic acid, the methyl group is separated, and the mass becomes resinised.

Eugenol, $C_{10}H_{12}O_2 = C_6H_3(OH)(OCH_3)(C_3H_5)$, (*Eugenic* or *Caryophyllic acid*), occurs in oil of cloves (from the flowers of *Caryophyllus aromaticus*), in oil of pimento (from *Myrtus pimenta*), and a few other volatile oils, and may be obtained therefrom by solution in potash, filtration, and precipitation by carbonic acid. It is a colourless, aromatic liquid, of sp. gr. 1·0779 at 0°, boiling at 247·5°, soluble in alcohol. Ferric chloride colours the solution blue. Eugenol, heated with hydriodic acid, gives off methyl iodide. By fusion with potash it is resolved into acetic acid and protocatechuic acid, $C_6H_3(OH)_2.CO_2H$. These reactions determine its constitution.

Eugenol dissolves in soda-ley, forming sodium-eugenol,—$C_6H_3(C_3H_5)(ONa)(OCH_3)$, which is converted by methyl iodide into methyl-eugenol, $C_6H_3(C_3H_5)(OCH_3)_2$, which, by oxidation with chromic acid mixture, yields dimethyl-protocatechuic acid, $C_6H_3(OCH_3)_2.CO_2H$. In like manner are formed ethyl-eugenol, propyl-eugenol, &c.

Coniferyl alcohol. $C_{10}H_{12}O_3 = C_6H_3(OH)(OCH_3).C_3H_4OH$, is formed by the decomposition of coniferin (see GLUCOSIDES) under the influence of emulsin. It crystallises in colourless prisms, melting at 74°–75°; is insoluble in cold water, slightly soluble in hot water, easily in ether and in alkalis. Dilute acids convert it into a resinous polymeride. By oxidation with chromic acid mixture it yields vanillin (p. 512).

Cholesterin, $C_{26}H_{44}O$, a product of the animal organism, is homologous with cinnyl alcohol, and has the characters of a monatomic alcohol. It is found in small quantity in various parts of the animal system, as in the bile, the brain and nerves, and the blood: it forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling, the cholesterin crystallises in brilliant colourless plates. It is a fatty substance, insoluble in water, tasteless, and inodorous; it is freely soluble in boiling alcohol and in ether, also in chloroform, and crystallises from the alcoholic solution in beautiful white laminæ having a mother-of-pearl lustre. It melts at 137°, and sublimes at 200°. On adding a solution of cholesterin in chloroform to strong sulphuric acid, the chloroform becomes purple-red, while the sulphuric acid below it exhibits a greenish-yellow fluorescence: the red chloroform solution evaporated in a porcelain capsule turns blue, green, and finally yellow.

Heated with strong sulphuric acid, it gives up water, and yields a resinous hydrocarbon, $C_{26}H_{42}$. With nitric acid it yields cholesteric acid, $C_8H_{10}O_5$, together with other products. With chlorine and bromine it forms substitution-products. Heated to 200° with acetic, butyric, benzoic, and stearic acids, it forms compound ethers. The *acetate* and *stearate* crystallise in needles, the former melting at 92°, the latter at 200°. The *benzoate* forms thick prisms, melting at 125°–130°. With PCl_5, or strong hydrochloric acid, it yields the *chloride*, $C_{26}H_{43}Cl$, which crystallises in needles, and is converted by ammonia into *cholesteramine*, $C_{26}H_{43}.NH_2$.

Isocholesterin, $C_{26}H_{44}O$, occurs, together with cholesterin, in the grease of sheep's wool, and may be separated by saponifying the fat, heating the mixture of cholesterin and isocholesterin thus obtained with benzoic acid, whereby they are converted into benzoic ethers, and crystallising these compounds from common ether, the cholesteryl benzoate separating in thick tabular crystals, the isocholesteryl benzoate in slender needles, and from the latter the isocholesterin may be obtained by heating with alcoholic potash. It crystallises from ether or acetone in slender needles, melting at 137°–138°. It does not give any colour reaction with chloroform and sulphuric acid, but in other respects it reacts like cholesterin. Its benzoic ether melts at 190°–191°.

AROMATIC ALDEHYDES.

1. ALDEHYDES ANALOGOUS TO MONATOMIC ACIDS.

Four aldehydes are known, belonging to the series $C_nH_{2n-8}O$, analogous to benzoic acid and its homologues, viz.:

Benzoic Aldehyde,	C_7H_6O
Toluic Aldehyde,	C_8H_8O
Cumic Aldehyde,	$C_{10}H_{12}O$
Sycocerylic Aldehyde,	$C_{18}H_{28}O$,

These aldehydes exhibit the same general reactions as those of the fatty series, and are obtained by similar processes.

Benzoic Aldehyde, Benzaldehyde, or **Bitter-almond oil,** $C_7H_6O = C_6H_5.CHO = C_7H_5O.H$, is produced—1. By the oxidation of benzyl alcohol. 2. By the action of nascent hydrogen on chloride or cyanide of benzyl:

$$C_6H_5.COCl + H_2 = HCl + C_6H_5.CHO.$$

3. By heating benzal chloride, $C_6H_5.CHCl_2$, with water to 130°-140°. 4. By heating benzyl chloride, $C_6H_5.CH_2Cl$, with an aqueous solution of lead nitrate. 5. By the oxidation of amygdalin with nitric acid. 6. By digesting bitter almonds with water for five or six hours at 30°-40°. The synaptase present then acts as a ferment on the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid (see GLUCOSIDES).

7. Benzoic aldehyde is formed, together with many other products, by the action of a mixture of manganese dioxide and sulphuric acid on albumin, fibrin, casein, and gelatin.

Pure benzoic aldehyde is a thin, colourless liquid, of great refractive power, and peculiar, very agreeable odour: its density is 1·050 at 15°, and its boiling point 180°: it is soluble in about 30 parts of water, and miscible in all proportions with alcohol and ether. Exposed to the air, it rapidly absorbs oxygen, and is converted into crystallised benzoic acid. Heated with solid *potassium hydroxide,* it gives off hydrogen, and yields potassium benzoate. With the *alkaline bisulphites* it forms beautiful crystalline compounds. The vapour of the oil is inflammable, and burns with a bright flame and much smoke.

Benzoic aldehyde, treated with *sodium amalgam,* is converted into benzyl alcohol, C_7H_8O. With *phosphorus pentachloride* it yields benzal chloride, $C_7H_6Cl_2$:

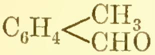
$$C_6H_5.CHO + PCl_5 = PCl_3O + C_6H_5.CHCl_2.$$

Ammonia converts it into hydrobenzamide, a white crystalline neutral body, which, when boiled with aqueous potash, is converted into an isomeric basic compound called amarine:

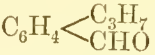
$$3C_7H_6O + 2NH_3 = (C_7H_6)_3N_2 + 3H_2O.$$

All the aromatic aldehydes act with ammonia in a similar manner, and are thereby distinguished from the fatty aldehydes.

Amarine and hydrobenzamide yield by dry distillation an isomeric base, $C_{21}H_{18}N_2$, called **lophine**, which crystallises in long, sparingly soluble needles, melting at 290°, and unites with acids, forming crystalline salts.

Toluic Aldehyde, C_8H_8O =  $C_6H_4{<}\substack{CH_3\\CHO}$ (1 : 4), is produced by distilling a mixture of the calcium-salts of *para*-toluic and formic acids. The oily distillate agitated with acid sodium sulphite, forms a crystalline compound, which, when distilled with sodium carbonate, yields the aldehyde, as an oil having a peppery odour, and boiling at 204°. On exposure to the air, it is gradually converted into para-toluic acid, $C_8H_8O_2$. With alcoholic potash it forms potassium para-toluate and para-xylyl alcohol:

$$2C_8H_8O + KOH = C_8H_7KO_2 + C_8H_{10}O.$$

Cumic Aldehyde, $C_{10}H_{12}O$ =  $C_6H_4{<}\substack{C_3H_7\\CHO}$ (1 : 4), exists, together with cymene, $C_{10}H_{14}$, in the essential oil of cumin, and in that of water-hemlock (*Cicuta virosa*), and may be obtained by agitating either of these oils with acid sodium sulphite, which takes up the cumic aldehyde, but not the cymene, and forms a crystalline compound, from which the aldehyde may be separated by distillation with potash. Cumic aldehyde is a colourless or slightly yellow liquid, having a powerful odour, and boiling at 237°. It is easily oxidised in the air, so that it must be distilled in a current of carbonic acid gas. It is converted into cumic acid, $C_{10}H_{12}O_2$, by oxidation, and by alcoholic potash into potassium cumate and cymyl alcohol, $C_{10}H_{14}O$.

Sycocerylic Aldehyde, $C_{18}H_{28}O$, is produced in thin prisms by oxidising sycoceryl alcohol with aqueous chromic acid.

Cinnamic Aldehyde, C_9H_8O.—This compound, which is the only known member of the series of aldehydes $C_nH_{2n-10}O$, constitutes the essential part of the volatile oils of cinnamon and cassia, which are obtained from the bark of different trees of the genus *Cinnamomum*, order *Lauraceæ*—viz., oil of cinnamon from Ceylon cinnamon, and oil of cassia from Chinese cinnamon. The aldehyde may be separated from these oils by means of acid potassium sulphite. It is produced artificially by oxidation of styryl alcohol; by dry distillation of a mixture of cinnamate and formate of calcium, and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid:

$$C_6H_5.CHO + CH_3.CHO = H_2O + C_6H_5.CH{=}CH.COH.$$

This last reaction is analogous to the formation of crotonic aldehyde by condensation of acetaldehyde (p. 255).

Cinnamic aldehyde, is a colourless oil, rather heavier than water. It may be distilled without alteration in a vacuum, or with de-aërated water, but absorbs oxygen quickly on exposure to the air, and passes into cinnamic acid. When fused with potash, it forms potassium cinnamate, and gives off hydrogen: $C_9H_8O + KOH = C_9H_7KO_2 + H_2$. Ammonia gas converts it into hydrocinnamide: $3C_9H_8O + 2NH_3 = (C_9H_8)_3N_2 + 3H_2O$.

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2. ALDEHYDES ANALOGOUS TO DIATOMIC AND MONOBASIC ACIDS.

Salicylic Aldehyde or **Salicylal,** $C_7H_6O_2 = C_6H_4{<}^{OH}_{CHO}$, (1:2) *Oxybenzaldehyde,* formerly called *Salicylous Acid.*—This compound occurs in herbaceous Spiræas, especially in the flowers of meadow-sweet (*Spiræa ulmaria*). It is formed artificially by oxidising saligenin, $C_6H_4(OH).CH_2OH$ (p. 505), or its glucosides, salicin and populin (see GLUCOSIDES), and together with the isomeric para-compound, by the action of chloroform on an alkaline solution of phenol:

$$C_6H_5(OH) + CHCl_3 + H_2O = 3HCl + C_6H_4(OH).CHO.$$

This last reaction affords the easiest method of preparing salicylal. Chloroform (3 parts) is gradually added, with agitation, to a solution of phenol (2 parts) and sodium hydroxide (4 parts) in 6–7 parts of water at 50°–60°, in a vessel with reversed condenser; and a quantity of water is added, sufficient to form (after heating to 60° for half an hour) a clear red-brown liquid, which is to be kept boiling for two hours, then acidulated and distilled. Salicylal and phenol then pass over, while para-oxybenzaldehyde remains behind. The distillate is shaken with ether, and the salicylic aldehyde is separated from the ethereal solution by agitation with acid sodium sulphite.

Salicylal is a thin, colourless, fragrant oil, acquiring a red tint by exposure to the air. It has a specific gravity of 1·1725 at 15°, solidifies at −20°, boils at 196°, and burns with a bright smoky flame. Water dissolves a perceptible quantity of salicylal, acquiring its fragrant odour, and the property (likewise exhibited by salicylic acid) of producing a deep violet colour with ferric salts. Alcohol and ether dissolve it in all proportions.

Salicylal is oxidised to salicylic acid by boiling with cupric oxide in alkaline solution, partly also by potassium dichromate and sulphuric acid; it likewise reduces silver oxide. When heated with potassium hydroxide, it is converted into potassium salicylate, with evolution of hydrogen:

$$C_7H_6O_2 + KOH = C_7H_5KO_3 + H_2.$$

By nascent hydrogen it is converted into saligenin, $C_7H_8O_2$; by ammonia into hydrosalicylamide:

$$3C_7H_6O_2 + 2NH_3 = 3H_2O + C_{21}H_{18}O_3N_2.$$

Salicylal is attacked by chlorine and bromine, forming $C_7H_5ClO_2$ and $C_7H_5BrO_2$, both of which are crystalline bodies, having acid properties. With moderately strong nitric acid it forms nitrosalicylal, $C_7H_5(NO_2)O_2$, which is also crystallisable, and forms crystallisable salts. With PCl_5 at ordinary temperatures salicylal forms orthoxybenzal chloride, $C_6H_4(OH).CHCl_2$, crystallising in prisms, and melting at 82°; and when heated with PCl_5, it yields orthochlorobenzal chloride, $C_6H_4Cl.CHCl_2$, a liquid boiling at 227°–230°, and isomeric with parachlorobenzal chloride from toluene (p. 439).

Salicylal dissolves in alkalis, forming crystalline compounds, formerly called *salicylites.* The *potassium compound*, $C_6H_4(OK).CHO$, forms square plates, easily soluble in water and in alcohol, and decomposing quickly when exposed in the moist state to the air.

Methyl-salicylal, $C_6H_4(OCH_3).CHO$, obtained by the action of methyl iodide on potassium salicylal, is a liquid boiling at 238°. Ethyl-salicylal, prepared in like manner, boils at 248°.

Acetyl-salicylal, $C_9H_8O_3 = C_6H_4(OC_2H_3O).CHO$, metameric with coumaric acid (*q.v.*), is formed by the action of acetic anhydride on sodium-salicylal at ordinary temperatures: $C_6H_4(ONa).CHO + (C_2H_3O)_2O = C_2H_3O.ONa + C_6H_4(OC_2H_3O).CHO$. The acetic oxide is added to an equivalent quantity of powdered anhydrous sodium-salicylal suspended in pure dry ether, and after the whole has stood for twenty-four hours, the ethereal liquid is filtered off from the sodium acetate, then evaporated, and the crystalline cake which separates on cooling, is purified by pressure between bibulous paper, and crystallisation from alcohol. Acetosalicylal thus prepared melts at 37°, boils at about 253°, and distils without decomposition. It forms definite compounds with alkaline bisulphites. It is decomposed by alcoholic potash, with formation of potassium acetate and potassium-salicylal:

$$C_6H_4(C_2H_3O)O.CHO + 2KOH = C_6H_4KO.CHO + C_2H_3KO_2 + H_2O.$$

Acetosalicylal likewise unites directly with acetic oxide.

If the product of the action of acetic oxide on salicylal, instead of being treated in the manner above described, be poured into water after a few minutes' boiling, an oily liquid sinks to the bottom, and sodium acetate remains in solution; and on distilling this oil, and collecting apart that which passes over after the temperature has risen to 290°, a crystalline substance is obtained, having the composition of *acetosalicylal minus one molecule of water*: this substance is identical in every respect with coumarin or coumaric anhydride,* the odoriferous principle of the Tonka bean (see COUMARIC ACID).

Paraoxybenzaldehyde, $C_6H_4(OH).CHO$ (1:4), is produced, together with salicylic aldehyde, by the action of chloroform on phenol dissolved in caustic soda (p. 510), and may be extracted by ether from the filtered residue of the distillation, and purified by recrystallisation from water. It forms stellate groups of slender needles; melts at 115°–116°; sublimes without decomposition, dissolves sparingly in cold, more readily in hot water, easily in alcohol and ether. Ferric chloride colours its solution dingy violet. It forms easily soluble compounds with alkaline bisulphites.

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* Perkin, Chem. Soc. Jour. 1868, p. 181.

Anisaldehyde or **Methyl-paraoxybenzaldehyde,** $C_6H_4(OCH)_3.CHO$, isomeric with methyl-salicylal, is formed, together with anisic acid, by oxidation of anisic alcohol, $C_8H_{10}O_2$, in contact with platinum black; also by the oxidising action of dilute nitric acid on the volatile oils of anise, fennel, and tarragon, which contain anethol, $C_{10}H_{12}O$. The product of the oxidation is shaken up with acid sodium sulphite, and the resulting crystalline compound is decomposed by solution of sodium carbonate.

Anisaldehyde is a colourless oil, having an aromatic odour and burning taste, a density of 1·123 at 15°, and boiling at 248°. It is nearly insoluble in water, but soluble in all proportions in alcohol and ether. It is converted by oxidation into anisic acid, $C_8H_8O_3$; by nascent hydrogen into anisic alcohol, $C_8H_{10}O_2$; and forms crystalline compounds with alkaline bisulphites. *Ammonia* converts it into anishydramide, $C_{24}H_{24}O_3N_2$. By *alcoholic potash* it is decomposed in the same manner as benzoic aldehyde, yielding potassium anisate and anisic alcohol:

$$2C_8H_8O_2 + KOH = C_8H_7KO_3 + C_8H_{10}O_2.$$

3. ALDEHYDES ANALOGOUS TO MONOBASIC AND TRIATOMIC ACIDS.

Dioxybenzaldehyde or **Protocatechuic Aldehyde,** $C_7H_6O_3 = C_6H_3(OH)_2.CHO(CHO : OH : OH : = 1 : 3 : 4)$, produced by the action of chloroform on an alkaline solution of pyrocatechin:

$$C_6H_4(OH)_2 + CHCl_3 + H_2O = C_6H_3(OH)_2.CHO + 3HCl;$$

also by boiling dichloropiperonal with water, and by heating vanillin or piperonal with dilute hydrochloric acid to 200°. Flat shining crystals, melting at 150°, easily soluble in water. The aqueous solution is coloured deep green by ferric chloride; by fusion with potash, the aldehyde is converted into protocatechuic acid.

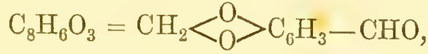
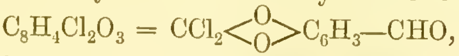
Vanillin, $C_8H_8O_3 = C_6H_3(OCH_3)_2.CHO$, *Methyl-protocatechuic Aldehyde*, is the odoriferous principle of vanilla (the fruit of *Vanilla aromatica*), in which it exists to the amount of about 2 per cent. It is produced artificially from coniferin, $C_{16}H_{22}O_8$, a glucoside occurring in the cambial secretion of all coniferous plants, by oxidation with chromic acid mixture; or the coniferin may be resolved by boiling with dilute acids, or by the action of emulsin, into glucose and coniferyl alcohol (p. 507):

$$C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3,$$

and the coniferyl alcohol oxidised by chromic acid mixture. Vanillin is also produced (similarly to protocatechuic aldehyde) by the action of chloroform on an alkaline solution of guaiacol (methyl-pyrocatechin, (p. 490).

Vanillin crystallises in stellate groups of colourless needles, melts at 80°–81°, and sublimes when cautiously heated; dissolves sparingly in cold, more freely in hot water, easily in alcohol and ether. It forms crystalline compounds with bases. When boiled with dilute hydrochloric acid, it is resolved into methyl chloride and protocatechuic aldehyde; and when fused with potash, it is converted, by oxidation of the aldehyde-group CHO, and separation of the methyl-group, into protocatechuic acid. Bromine converts it into bromovanillin, $C_8H_7BrO_3$, which crystallises in yellowish laminæ melting at 161°.

Dimethyl-protocatechuic Aldehyde, or Methyl-vanillin, $C_6H_3(OCH_3)_2.CHO$, and Ethyl-methyl-protocatechuic Aldehyde, or Ethyl-vanillin, $C_6H_3(OCH_3)(OC_2H_5).CHO$, are formed by the action of methyl iodide or ethyl iodide on potassium-vanillin. Both crystallise in colourless prisms, slightly soluble in cold water, somewhat more easily in alcohol and ether. The former melts at 15°–20°, and boils at 285°; the latter melts at 64°–65°, and easily sublimes.

Piperonal,  $C_8H_6O_3 = CH_2{<}\substack{O\\O}{>}C_6H_3{-}CHO$, *Methene-protocatechuic Aldehyde,* is obtained by distilling a dilute solution of potassium piperate with potassium permanganate, and agitating the distillate with ether. It forms long, colourless, shining crystals, having a very pleasant odour; melts at 37°, boils at 263°; dissolves sparingly in cold, more freely in hot water, easily in alcohol and ether; unites with acid sulphites of alkali-metal. Heated with 3 mol. PCl_5, it yields liquid dichloropiperonal chloride, $C_8H_4Cl_4O_3$, which is resolved by cold water into hydrochloric acid and dichloropiperonal,  $C_8H_4Cl_2O_3 = CCl_2{<}\substack{O\\O}{>}C_6H_3{-}CHO$, and by boiling with water into CO_2 and protocatechuic aldehyde.

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4. ALDEHYDES ANALOGOUS TO BIBASIC ACIDS.

Phthalic Aldehyde, $C_8H_6O_2 = C_6H_4(CHO)_2$ (1:2), is formed by treating phthalyl chloride, $C_8H_4O_2Cl_2$, with zinc and hydrochloric acid, or by dissolving magnesium in a cooled solution of phthalyl chloride, and may be extracted by neutralising the solution with sodium carbonate and agitating with ether. It crystallises from hot water in small colourless rhombic tables, melts at 65°, and sublimes when cautiously heated; dissolves sparingly in cold, more readily in boiling water, easily in alcohol and ether.

Terephthalic Aldehyde (1:4), is formed by prolonged boiling of tollylene chloride (p. 441) with water (20 parts) and lead nitrate (1 part), and subsequent distillation. Crystallises in slender needles, melting a 114°–115°.

Both these aldehydes dissolve sparingly in cold, more readily in boiling water, easily in alcohol; the ortho-compound is moderately soluble, the para-compound easily soluble in ether. Both form crystalline compounds with acid sodium sulphite.

KETONES.

The aromatic ketones may contain either two aromatic alcohol-radicles (phenyl and its homologues), or one aromatic radicle, and one alcohol-radicle (methyl, &c.) belonging to the fatty series. The latter only will be noticed in this place, the former in connection with the diphenyl-compounds.

Phenyl-methyl Ketone or **Acetophenone,** $C_6H_5.CO.CH_3$, is formed by distilling a mixture of benzoate and acetate of calcium, or by the action of zinc-methyl on benzoyl chloride:

$$2(C_6H_5.CO.Cl) + Zn(CH_3)_2 = ZnCl_2 + 2(C_6H_5.CO.CH_3).$$

It crystallises in large laminæ melting at 14°, is converted by nascent hydrogen into phenyl-ethyl alcohol (p. 503), and resolved by oxidation with chromic acid into benzoic acid and carbon dioxide.

Phenyl-ethyl Ketone or **Propiophenone,** $C_6H_5.CO.C_2H_5$, from benzoate and propionate of calcium, and by the action of zinc-ethyl on benzoyl chloride, is a liquid which boils at 208°–210°, is converted by nascent hydrogen into secondary phenyl-propyl alcohol, and resolved by chromic acid into benzoic and acetic acids.

Phenyl-propyl Ketone and **Phenyl-isopropyl Ketone,** $C_6H_5.CO.C_3H_7$, are formed by distilling a mixture of calcium benzoate and butyrate or isobutyrate respectively. The former boils at 220°–222°, and is oxidised by chromic acid to benzoic and propionic acids; the latter boils at 215°, and is oxidised by chromic acid to benzoic, acetic, and carbonic acids.

Benzyl-methyl Ketone, $C_6H_5.CH_2.CO.CH_3$, formed by distillation of alphatoluate (phenyl-acetate) and acetate of calcium, and by the action of zinc-methyl on alphatoluic chloride, boils at 214°–216°, unites with acid sodium sulphite, and is oxidised by chromic acid to benzoic and acetic acids.

Benzyl-ethyl Ketone, $C_6H_5.CH_2.CO.C_2H_5$, from alphatoluic chloride with zinc-ethyl, boils at 226°, and is oxidised by chromic acid to benzoic and propionic acids.

AROMATIC ACIDS.

1. MONATOMIC ACIDS, $C_nH_{2n-8}O_2$.

These acids, which bear the same relation to the hydrocarbons homologous with benzene that the fatty acids, $C_nH_{2n}O_2$, bear to the paraffins, C_nH_{2n+2}, are produced by reactions analogous to some of those which yield the fatty acids, viz.:

1. By oxidation of the corresponding aldehydes and alcohols: thus benzoic acid, $C_7H_6O_2$ or $C_6H_5.COOH$, is formed by oxidation of benzaldehyde, $C_6H_5.COH$, and of benzyl alcohol, $C_6H_5.CH_2OH$.

2. By the action of water on the corresponding acid chlorides.

3. By the action of acids or alkalis at the boiling heat on the aromatic nitrils (cyanides of phenyl and its homologues, p. 441):

$$\underset{\text{Phenyl cyanide.}}{C_6H_5CN} + 2H_2O = NH_3 + \underset{\text{Benzoic acid.}}{C_6H_5.CO_2H}$$

Benzoic acid and its homologues are likewise obtained by the following processes:

4. By the action of sodium and carbon dioxide on the monobrominated derivatives of benzene and its homologues; *e.g.*,

$$\underset{\text{Bromobenzene.}}{C_6H_5Br} + Na_2 + CO_2 = NaBr + \underset{\text{Sodium benzoate.}}{C_6H_5.CO_2Na}$$

$$\underset{\text{Bromotoluene.}}{C_6H_4Br.CH_3} + Na_2 + CO_2 = NaBr + \underset{\text{Sodium toluate.}}{C_6H_4(CH_3).CO_2Na}$$

5. By oxidation of the hydrocarbons homologous with benzene by means of chromic acid mixture or dilute nitric acid. By chromic acid the lateral chains, CH_3, $CH_2.CH_3$, &c., are at once oxidised to CO_2H; and the hydrocarbons which contain only one lateral chain, $C_6H_5.CH_3$, $C_6H_5.C_2H_5$, &c., are all oxidised to benzoic acid, while those which contain two lateral chains are converted into acids containing two carboxyl-groups (di-carbon acids), the xylenes, $C_6H_4(CH_3)_2$, for example, into phthalic acids, $C_6H_4(CO_2H)_2$. With dilute nitric acid, on the other hand, monocarbon acids are produced, at least in the first instance, the xylenes, for example, yielding toluic acids, $C_6H_4(CH_3).CO_2H$.

For oxidation with chromic acid, 40 grams of potassium dichromate are mixed with 37 grams of strong sulphuric acid diluted with 2 to 3 vol. water; to this mixture 10–20 parts of the hydrocarbon are added, and the whole is boiled for some time in a flask provided with a long upright condensing tube, till all the chromic acid is reduced and the solution has aquired a pure green colour. The product is then diluted with water, boiled with solution of sodium carbonate, and the organic acid is precipitated from the filtrate by hydrochloric acid.

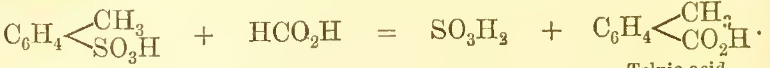
With the proportions above mentioned the reaction takes place according to the equation:

$$Cr_2O_7K_2 + 4SO_4H_2 = (SO_4)_3Cr_2 + SO_4K_2 + 4H_2O + O_3,$$

the three atoms of oxygen thus liberated serving for the oxidation of the hydrocarbon.

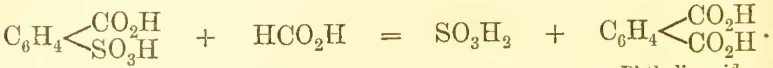
For oxidation with nitric acid, the hydrocarbon is boiled for two or three days with ordinary nitric acid diluted with 3 parts of water in a flask with a vertical condensing tube. To remove the nitro-acids formed at the same time, the crude product is heated with tin and strong hydrochloric acid, whereby the nitro-acids are converted into amido-acids, which dissolve in the hydrochloric acid.

6. By fusing the sulpho-acids of the aromatic hydrocarbons, or the sulpho-aromatic acids, with potassium formate:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H} \quad + \quad HCO_2H \quad = \quad SO_3H_2 \quad + \quad C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{CO_2H} \, .$$

Toluene-sulphonic acid. Toluic acid.



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO_2H}{SO_3H} \quad + \quad HCO_2H \quad = \quad SO_3H_2 \quad + \quad C_6H_4{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} \, .$$

Sulphobenzoic acid. Phthalic acid.

The aromatic acids occur, either free or combined, in many resins and balsams and in the animal organism.

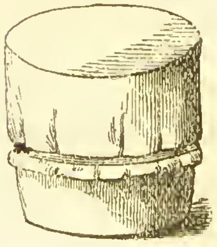
Benzoic Acid, $C_7H_6O_2 = C_6H_5.CO_2H$.—This acid, the analogue of benzyl alcohol, is produced by the first four of the general methods above mentioned, and by boiling hippuric acid (benzoyl-glycocine) or the urine of cows or horses, which contains that acid, with strong hydrochloric acid:

$$CH_2(NH.C_7H_5O).CO_2H + H_2O = CH_2(NH_2).CO_2H + C_7H_5O.OH\,.$$

Benzoyl-glycocine. Glycocine. Benzoic acid.

This process is applied to the preparation of benzoic acid on the large scale. Benzoic acid is also produced by the oxidation of a great variety of organic bodies, as toluene, cumene, cinnamic aldehyde, cinnamic acid, cinnamene, casein, gelatin, &c.

Fig. 17.



Benzoic acid exists ready-formed in several balsams and gum-resins, especially in gum-benzoin, which exudes from the bark of *Styrax Benzoin*, a tree growing in Sumatra, Java, Borneo, and Siam. From this substance the benzoic acid may be extracted by sublimation in an iron pan (fig. 17), having a sheet of bibulous paper pierced with pin-holes stretched over its mouth, and covered with a cap of stout paper. A more productive method is to boil the powdered benzoin with slaked lime and water, and decompose the filtered and concentrated solution of calcium benzoate with hydrochloric acid. The benzoic acid thus precipitated may be purified by sublimation.

Benzoic acid is inodorous when cold, but acquires a faint smell when gently warmed; it melts at 120°, and sublimes at a temperature a little above; boils at 250°. It dissolves in about 200 parts of cold and 25 parts of boiling water, and with great facility in alcohol. Benzoic acid is not affected by ordinary nitric acid, even at boiling heat; but with *fuming nitric acid* it forms a substitution-product.—*Chlorine* also acts on benzoic acid, forming substitution-products. — *Phosphorus pentachloride* converts it into benzoyl chloride, C_7H_5OCl.—Benzoic acid dissolves in ordinary strong sulphuric acid, but is precipitated unaltered on addition of water. By fuming sulphuric acid, however, and still more readily by sulphuric oxide, it is converted into sulphobenzoic acid, $C_7H_6SO_5$, (p. 527). By nascent hydrogen (evolved by sodium amalgam) it is partly reduced to benzoic aldehyde and benzylic alcohol, and is partly converted, by addition of hydrogen, into hydrobenzoic acid, $C_7H_{10}O_2$, a crystalline acid which forms a crystalline calcium salt, $Ca(C_7H_9O_2)_2$, and, when recrystallised either in the free state or in the form of calcium salt, is ultimately converted by oxidation into benzoic acid; its ethylic ether, $C_2H_5.C_7H_9O_2$, has the odour of ethyl valerate.

All the benzoates are more or less soluble: they are easily formed, either directly or by double decomposition. The *benzoates of the alkalis* and of *ammonia* are very soluble, and somewhat difficult to crystallise.—*Calcium benzoate* forms groups of small colourless needles, which require 20 parts of cold water for solution; the *barium salt* dissolves with difficulty in the cold. Neutral *ferric benzoate* is a soluble compound; but the basic salt obtained by neutralising as nearly as possible with ammonia a solution of ferric oxide, and then adding ammonium benzoate, is quite insoluble. Iron is sometimes thus separated from other metals in quantitative analysis. Neutral and basic *lead benzoate* are freely soluble in the cold. *Silver benzoate* crystallises in thin transparent plates, which blacken on exposure to light.

Calcium benzoate is resolved by dry distillation into calcium carbonate and benzone, or benzophenone, $C_{13}H_{10}O$, the ketone of benzoic acid $(C_7H_5O_2)_2Ca = CO_3Ca + CO(C_6H_5)_2$. On the other hand, benzoic acid, distilled with excess of lime, is resolved into carbon dioxide and benzene: $C_7H_6O_2 = CO_2 + C_6H_6$.

Benzoic Chloride, or **Benzoyl Chloride,** C_7H_5OCl, is prepared by the action of phosphorus pentachloride on benzoic acid. It is a colourless liquid of disagreeable pungent odour; sp. gr. 1·106; boiling point, 199°. The vapour is inflammable, and burns with a greenish flame. Benzoyl chloride is decomposed, slowly by cold and quickly by boiling water, into benzoic and hydrochloric acids; with an alkaline hydroxide, a benzoate and chloride of the alkali-metal are produced.

Benzoyl cyanide, $C_6H_5.CO.CN$, obtained by distilling the chloride with potassium cyanide, crystallises in large plates, melts at 31°, and boils at 206°–208°. By boiling with alkalis, it is resolved into benzoic and hydrocyanic acids.

Benzoic Oxide, or **Anhydride,** $C_{14}H_{10}O_3$ or $(C_7H_5O)_2O$, is obtained by the action of benzoyl chloride on potassium benzoate:

$$C_7H_5O(OK) + C_7H_5OCl = KCl + (C_7H_5O)_2O.$$

Benzoyl chloride acts in like manner on acetate or valerate of sodium, forming aceto-benzoic or valero-benzoic oxide, either of which splits up on distillation into acetic or valeric oxide and benzoic oxide; *e.g.*,

$$C_7H_5OCl + C_5H_9O(ONa) = NaCl + (C_7H_5O)(C_5H_9O)O,$$

and $$2(C_7H_5O)(C_5H_9O)O = (C_7H_5O)_2O + (C_5H_9O)_2O.$$

Benzo-œnanthylic, benzostearic, benzo-angelic, benzo-cuminic oxide, and several others, have been obtained by similar processes.

Benzoic oxide crystallises in oblique rhombic prisms, melting at 42°, and distilling undecomposed at 310°. It melts in boiling water, remaining fluid for a long time, but is ultimately converted into benzoic acid, and dissolves: caustic alkalis effect the conversion much more rapidly. With ammonia it forms ammonium benzoate and benzamide:

$$(C_7H_5O)_2O + 2NH_3 = C_7H_5O(NH_4)O + C_7H_5O.NH_2.$$

Benzoyl Dioxide, or Peroxide, $C_{14}H_{10}O$, or $(C_7H_5O)_2O_2$.—Brodie obtained this compound by bringing benzoyl chloride in contact with barium dioxide under water; the product, when recrystallised from ether, yields large shining crystals of benzoyl dioxide, which explode when heated. Boiled with potash-solution, it gives off oxygen, and forms potassium benzoate.

Thiobenzoic Acid, $C_6H_5.CO.SH$, formed by the action of benzoyl chloride on alcoholic potassium sulphide, is crystalline, melts at 24°, and distils with aqueous vapour. Its ethylic ether boils at 243°.

Benzoyl monosulphide, $(C_7H_5O)_2S$, formed by the action of benzoyl chloride on thiobenzoic acid, crystallises from ether in large prisms, melting at 48°, and distilling without decomposition. The disulphide, $(C_7H_5O)_2S_2$, produced by oxidation of thiobenzoic acid when its ethereal solution is exposed to the air, forms shining crystals melting at 128°.

Dithiobenzoic acid, $C_6H_5.CS.SH$, is formed by boiling the compound $C_6H_5.CCl_3$ with an alcoholic solution of potassium sulphide:

$$C_6H_5.CCl_3 + 2K_2S = 3KCl + C_6H_5.CS.SK.$$

The free acid is very unstable: its lead salt crystallises from carbon sulphide in red needles.

Benzamide, $C_7H_7NO = C_6H_5.CO.NH_2$, is formed (similarly to acetamide, p. 379) by the action of aqueous ammonia on benzoyl chloride or ethyl benzoate; also by oxidising hippuric acid with lead dioxide:

$$C_9H_9NO_3 + O_3 = C_7H_7NO + 2CO_2 + H_2O.$$

Benzamide crystallises in nacreous laminæ, nearly insoluble in cold water, easily soluble in boiling water, also in alcohol and ether; it melts at 125°, and volatilises undecomposed between 286° and 290°. Its reactions are for the most part similar to those of acetamide. Heated with benzoic oxide or chloride, it yields benzonitril and benzoic acid:

$$\underset{\text{Benzamide.}}{C_7H_7NO} + \underset{\text{Benzoic oxide.}}{(C_7H_5O)_2O} = \underset{\text{Benzonitril.}}{C_7H_5N} + \underset{\text{Benzoic acid.}}{2C_7H_6O_2},$$

$$\underset{\text{Benzamide.}}{C_7H_7NO} + \underset{\text{Benzoic chloride.}}{C_7H_5OCl} = \underset{\text{Benzonitril.}}{C_7H_5N} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + HCl.$$

Heated with fuming hydrochloric acid, it forms hydrochloride of benzamide, $C_7H_7NO.HCl$, which separates on cooling in long aggregated prisms. Its aqueous solution dissolves mercuric oxide, forming benzomercuramide, $C_6H_5.CO.NHg$. By distillation with PCl_5 or P_2S_5, it is converted into benzonitril.

Phenyl-benzamide, $C_6H_5.CO.NH(C_6H_5)$, is formed by the action of aniline on benzoyl chloride.

SUBSTITUTED BENZOIC ACIDS.

The action of chlorine and bromine on benzoic acid gives rise for the most part only to mono-substituted derivatives, $C_6H_4X.CO_2H$, belonging to the meta-series (Cl or Br and CO_2H, in the relative positions 1, 3); with nitric acid (diluted with 3 parts of water) meta-derivatives are also produced, together with small quantities of the ortho- and para-compounds. These and all the other mono-halogen- and mono-nitro-derivatives of benzoic acid may also be formed by oxidation of the corresponding derivatives of toluene; *e.g.*,

$$C_6H_4Br.CH_3 + O_3 = C_6H_4Br.CO_2H + H_2O;$$

the meta- and para-compounds by chromic acid, the ortho-compounds by dilute nitric acid; these last compounds are attacked with difficulty by chromic acid, and then completely broken up.

The halogen-derivatives of benzoic acid may also be formed from the corresponding amidobenzoic acids, by substitution of Cl, &c., for NH_2, through the medium of the diazo-compounds; and the monochlorine- and monobromine-derivatives by treating the corresponding oxy-acids, $C_6H_4(OH).CO_2H$ with PCl_5 or PBr_5, and decomposing the resulting chloride or bromide with water; *e.g.*,

$$C_6H_4(OH).CO.OH + PCl_5 = C_6H_4Cl.CO.Cl + PCl_3O + H_2O,$$

$$\text{and} \quad C_6H_4Cl.CO.Cl + HOH = C_6H_4Cl.CO.OH + HCl.$$

The ortho-derivatives of benzoic acid fuse at lower temperatures than the corresponding meta- and para-derivatives. They are moderately soluble in water, and form easily soluble barium salts, by means of which they may be separated from the meta- and para-derivatives.

Monochlorobenzoic Acids, $C_7H_5ClO_2$.—The *ortho*-compound, $C_6.CO_2H.Cl.H_4$ (*Chlorosalylic acid*), prepared by treating salicylic acid (*o*-oxybenzoic acid) with PCl_5, and decomposing the resulting chloride with boiling water, crystallises in colourless needles, melts at 137°, also under boiling water, and is more soluble in water than the meta- and para-compounds.

The *meta*-compound, $C_6.CO_2H.H.Cl.H_3$, is formed by oxidation of meta-chlorotoluene; by heating benzoic acid with hydrochloric acid and manganese dioxide or potassium chlorate, or with solution of bleaching powder, or with antimonic chloride; also by decomposition of chlorohippuric acid; and from (1:4) chloronitrobenzene by means of potassium cyanide. It crystallises in colourless needles, melting without decomposition at 152°, very slightly soluble in boiling water.

The *para*-compound, $C_6.CO_2H.H.H.Cl.H_2$ (*Chlorodracylic acid*), formed by oxidation of (1:4) chlorotoluene, sublimes in colourless scales, which melt at 236°-237°.

Dichlorobenzoic Acids, $C_6H_3Cl_2.CO_2H$.—Two modifications (out of six) are known, viz. (α.) 1:3:4 (CO_2H in 1), formed from benzoic acid, and from (1:3) or (1:4) chlorobenzoic acid by boiling with solution of bleaching powder, or by heating with antimonic chloride: also by oxidation of (1:3:4) dichlorotoluene with chromic acid. Colourless needles, melting at 202°, slightly soluble in water. (β.) (1:2:3), produced, like the α-acid, from (1:2) chlorobenzoic acid, and together with the α-acid, by treating benzoic acid with HCl and ClO_3K, or with solution of bleaching powder. The two acids may be separated by means of their barium salts, the β-salt being the more soluble of the two. The β-acid forms slender, shining needles, melts at 150°, boils at 301°, dissolves in about 1200 parts of water at 11°, more easily in boiling water.

Trichlorobenzoic acid, $C_6H_2Cl_3.CO_2H$, formed by oxidation of trichlorotoluene, crystallises in small needles melting at 163°, nearly insoluble in cold water. An isomeric acid, formed by heating dinitro-paramidobenzoic acid with fuming hydrochloric acid, melts at 203°, and sublimes without decomposition.

Monobromobenzoic acid, $C_6H_4Br.CO_2H$ (1:2), from ortho-bromotoluene with nitric acid, or from *o*-amidobenzoic acid by heating the diazoperbromide with HBr, sublimes in needles, and melts at 147°-148°. Its barium salt is very soluble in water. (1:3), or ordinary *bromobenzoic acid*, from metabromotoluene, and by heating benzoic acid with bromine and water to 120°-130°, sublimes in needles, and melts at 155°. (1:4) from parabromotoluene, is nearly insoluble in water, crystallises in needles, and melts at 251°.

Di-, tri-, and penta-bromobenzoic acids are formed by heating benzoic acid with bromine to 200° and above. $C_7H_4Br_2O_2$, (1:3:4), forms small needles melting at 229°-230°. $C_7H_3Br_3O_2$ and $C_7HBr_5O_2$ melt between 234° and 235°.

Mono-iodobenzoic Acids, $C_6H_4I.CO_2H$, are obtained by oxidation of iodotoluenes with nitric acid, or from the corresponding amidobenzoic acids by decomposing the diazo-compounds with hydriodic acid :

(1:2), form needles, melting at 157°; converted by fusion with potash into salicylic acid.

(1:3) sublimes in needles, melting at 187°; converted by fusion with potash into oxybenzoic acid.

(1:4) sublimes in scales, melts at about 267°, converted by fusion with potash into para-oxybenzoic acid.

Fluobenzoic acid, $C_6H_4F.CO_2H$, produced by treating diazo-amidobenzoic acid with hydrofluoric acid, crystallises in rhombic prisms melting at 182°.

Mononitrobenzoic Acids, $C_6H_4(NO_2).CO_2H$.—When benzoic acid is treated with fuming nitric acid, or better, with a mixture of nitre (2 parts) and strong sulphuric acid (3 parts) to 1 part of benzoic acid, the chief product obtained is metanitrobenzoic acid, the ortho-compound being formed in smaller, and the para- in very small quantity—the mass being warmed till it melts, and the liquid mass poured off from the solid potassium sulphate. The three nitro-acids are separated by the different solubilities of their barium-salts—that of the ortho-acid being very soluble, that of the meta-acid rather sparingly, and that of the para-acid very slightly soluble. Cinnamic acid yields by nitration two nitro-acids, $C_9H_7(NO_2)O_2$, *ortho-* and *para,* from which the corresponding nitrobenzoic acids may be obtained by oxidation. Hippuric acid yields by nitration a nitrohippuric acid, convertible into metanitrobenzoic acid.

(1:2) Nitrobenzoic acid crystallises in needles or prisms, soluble in 164 parts of water at 16·5°, melting at 145°. (1:3) Nitrobenzoic acid crystallises in needles or laminæ, dissolves in 425 parts of water at 16·5°, sublimes in white needles, melts at 142°. (1:4) Nitrobenzoic acid, formed also by oxidation of paranitrotoluene, crystallises in yellowish laminæ, very slightly soluble in water, melting at 240°.

Dinitrobenzoic Acids, $C_6H_3(NO_2)_2.CO_2H$.—Orthonitrobenzoic acid, treated with a mixture of nitric and sulphuric acids, yields three dinitrobenzoic acids (α, β, and γ), easily separated by the unequal solubility of their barium-salts—that of α being very slightly soluble in cold water, that of β moderately, and that of γ very easily soluble. The β-acid is also produced by oxidation of (1:2:4) dinitrotoluene (melting point 70·5°) with chromic acid. A fourth acid, δ, is obtained by the action of nitric and sulphuric acid on metanitrobenzoic acid.—α (1:2:5).* Colourless prisms, melting at 177°, moderately soluble in hot, sparingly in cold water. β. (1:2:4) Long rhombic plates or prisms melting at 179°. γ. (1:2:6) Slender, white felted needles, melting at 202°, resolved at a higher temperature into (1:3) dinitrobenzene and CO_2. δ. (1:3:5) Crystallises from water in large square plates; from alcohol in prisms.

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* CO_2H in 1.

By reduction with tin and HCl, the α- and δ-compounds yield the corresponding diamidobenzoic acids, whereas β and γ yield no diamido-acids, but (1:3) diamidobenzene and CO_2.

Nitro-chloro- and *Nitro-bromobenzoic acids* are obtained by nitration of chloro- and bromo-benzoic acids. (1:3), bromobenzoic acid, yields two nitrometabromobenzoic acids,—one melting at 248°, the other at 141°. In both of them the NO_2-group is in the ortho-position (2 or 6) with respect to the CO_2H, and both yield by reduction (1:2) amidobenzoic acid.

Amidobenzoic Acids, $C_6H_4(NH_2).CO_2H$.—The three modifications are formed by reduction of the three nitrobenzoic acids, best by gentle heating with tin and hydrochloric acid. At the end of the reaction the product is diluted with water, precipitated with excess of sodium carbonate, and the concentrated filtrate is acidulated with acetic acid. The ortho-compound is also produced by boiling indigo (1 part) for several days with soda-ley of specific gravity 1·38 (10 parts), gradually adding pulverised manganese dioxide, and renewing the water as it evaporates, till the colour of the mass has become light yellow. The product is then dissolved in water, the solution is neutralised with sulphuric acid, filtered, and evaporated to dryness; the residue is exhausted with alcohol; and the salt which remains after evaporation of the alcohol is dissolved in hot water and decomposed with acetic acid.

The three amidobenzoic acids react like glycocine (amidacetic acid), and yield well-characterised salts, both with metallic oxides and with acids. When heated above their melting points they are resolved into aniline and carbon dioxide.

Ortho- (*Anthranilic acid*).—Thin colourless prisms or laminæ, sparingly soluble in cold water, easily in hot water and in alcohol; melts at 144°. *Meta-*. Small colourless needles, united in nodular groups; easily soluble in hot, sparingly in cold water, melts at 173°–174°. *Para-* (*amidodracylic acid*). Long slender shining needles, easily soluble in water, melting at 186°–187°.

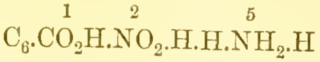
Nitro-amidobenzoic acids, $C_6H_3(NO_2){<}{\begin{smallmatrix}NH_2\\CO_2H\end{smallmatrix}}$.

1. *Nitro-orthamidobenzoic acid* is known in two modifications, viz.:

$$\underset{\alpha.\ (1:2:5)}{C_6.CO_2H.NH_2.H.H.NO_2.H} \qquad \underset{\beta.\ (1:2:6)}{C_6.CO_2H.NH_2.H.H.H.NO_2}$$

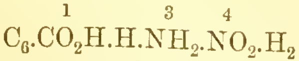
which are produced from the corresponding nitrosalicylic acids by heating their diethylic ethers with alcoholic ammonia, and decomposing the resulting nitramidobenzamides, $C_6H_3(NO_2)(NH_2).CO.NH_2$, with boiling baryta-water. Both acids crystallise in long needles, the α-acid melting at 270°, the β-acid at 205°.

2. *Nitro-metamidobenzoic acid* is known in three modifications, viz.:



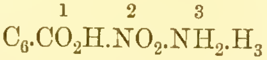
$$\overset{1}{C_6.CO_2H}.\overset{2}{NO_2}.H.H.\overset{5}{NH_2}.H$$

α



$$\overset{1}{C_6.CO_2H}.H.\overset{3}{NH_2}.\overset{4}{NO_2}.H_2$$

β



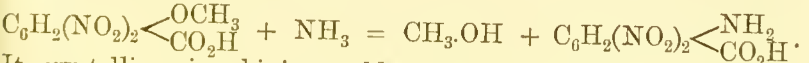
$$\overset{1}{C_6.CO_2H}.\overset{2}{NO_2}.\overset{3}{NH_2}.H_3$$

γ.

They are obtained by boiling the three dinitro-uramidobenzoic acids (p. 525) with water. All three crystallise in yellow needles; α and β sparingly soluble in hot water, γ easily soluble.

3. *Nitro-paramidobenzoic acid* (1 : 3 : 4), obtained in like manner from dinitro-para-uramidobenzoic acid, or by heating nitranisic acid with aqueous ammonia to 140°–170° for three or four hours, forms small deep yellow needles, slightly soluble in boiling water, melting at 284°.

Dinitro-paramidobenzoic acid, $C_6H_2(NO_2)_2{<}^{NH_2}_{CO_2H}$, or *Chrysanisic acid*, is produced by heating dinitro-anisic or dinitro-ethylparaoxybenzoic acid with aqueous ammonia, the group OCH_3 or OC_2H_5 being thus replaced by NH_2:



$$C_6H_2(NO_2)_2{<}^{OCH_3}_{CO_2H} + NH_3 = CH_3.OH + C_6H_2(NO_2)_2{<}^{NH_2}_{CO_2H}.$$

It crystallises in shining golden-yellow needles, melts at 259° and sublimes; is nearly insoluble in cold water, moderately soluble in boiling water and in alcohol. It is a strong monobasic acid.

Dinitro-orthoamidobenzoic acid, obtained in like manner from dinitro-ethylsalicylic acid, crystallises from alcohol, in which it is slightly soluble, in golden-yellow scales melting at 256°.

Acetyl-metamidobenzoic acid, $C_9H_9NO_3 = C_6H_4{<}^{NH.C_2H_3O}_{CO.OH}$, is formed by digesting (1 : 3) amidobenzoic acid with glacial acetic acid at 160°, or zinc metamidobenzoate with acetyl chloride at 100°:

$$(C_6H_4.NH_2.CO_2)_2Zn + 2C_2H_3OCl = ZnCl_2 + 2C_6H_4(NH.C_2H_3O)CO_2H,$$

It forms white microscopic crystals, insoluble in cold water and in ether, slightly soluble in boiling water, easily in boiling alcohol, melts at 226°–230°, sublimes at 200°. It is a monobasic acid, forming easily soluble salts with the metals of the alkalis and alkaline earths; sparingly soluble salts with lead, silver, and zinc. By boiling with dilute sulphuric acid, it is resolved into acetic and amidobenzoic acids:

$$C_9H_9NO_3 + H_2O = C_2H_4O_2 + C_7H_7NO_2.$$

Acetyl-paramidobenzoic acid, isomeric with the last, is easily obtained by oxidising acetoparatoluide, $C_6H_4(NH.C_2H_3O).CH_3$, with potassium permanganate. It crystallises in needles, sparingly soluble in water, more readily in alcohol, and melting with decomposition at about 250°.

Hippuric or Benzamidacetic acid, $C_9H_9NO_3 = CH_2<\begin{matrix}NH.C_7H_5O\\CO.OH\end{matrix}$ (*Benzoyl-glycocine*).—This acid, metameric with the two just described, is formed by the action of benzoyl chloride on the zinc-salt of amidacetic acid (glycocine):

$$(CH_2.NH_2.CO_2)_2Zn + 2C_7H_5OCl = ZnCl_2 + 2CH_2(NH.C_7H_5O)CO_2H,$$

the reaction being analogous to the second of those above given for the formation of acetamidobenzoic acid.

Hippuric acid occurs, often in large quantities, in the urine of horses, cows, and other herbivorous animals; in smaller quantity also in human urine. It may be prepared by boiling fresh cows' or horses' urine with milk of lime, and precipitating the concentrated filtrate with hydrochloric acid. For purification the crude acid is washed with chlorine-water; or its solution in dilute soda-ley is boiled with sodium hypochlorite till it becomes colourless, and the solution after cooling is precipitated with hydrochloric acid.

Hippuric acid crystallises in rhombic prisms, which have a slightly bitter taste and acid reaction, melt on the application of heat, and require for solution about 600 parts of cold water: it also dissolves in hot alcohol. At a high temperature it decomposes, yielding benzoic acid, ammonium benzoate, and benzonitril, with a coaly residue. Boiling hydrochloric acid converts it into benzoic acid and glycocine (amidacetic acid):

$$CH_2(NH.C_7H_5O).CO_2H + HOH = C_7H_5O.OH + CH_2(NH_2).CO_2H;$$

just as acetamidobenzoic acid is resolved into acetic and amidobenzoic acids.

Hippuric acid is monobasic, the formula of the hippurates of monatomic metals being $C_9H_8MNO_3$. Most metallic oxides dissolve readily in hippuric acid. The hippurates of potassium, sodium, and ammonium are very soluble, and difficult to crystallise; their solutions form a cream-coloured precipitate with ferric salts, and white curdy precipitates with silver nitrate and mercurous nitrate. A characteristic reaction of the hippurates is, that they give off ammonia when fused with excess of potash or lime, and yield benzene by distillation. Mineral acids decompose them, separating the hippuric acid.

Hippuric acid, treated with nitrous acid, gives off nitrogen, and is converted into benzoglycollic acid, $C_9H_8O_4$, an acid containing the elements of benzoic and glycollic (oxyacetic) acids, minus one molecule of water:

$$C_9H_9NO_3 + HNO_2 = C_9H_8O_4 + H_2O + N_2;$$

and benzoglycollic acid, when boiled with water, splits up into benzoic and glycollic acids:

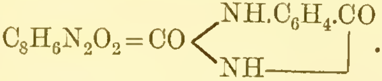
$$C_9H_8O_4 + H_2O = C_7H_6O_2 + C_2H_4O_3.$$

If, in the preparation of hippuric acid, the urine be in the slightest degree putrid, the hippuric acid is all destroyed during the evaporation, ammonia is disengaged in large quantity, and the liquid is then found to yield nothing but benzoic acid, not a trace of which can be discovered in the unaltered secretion. When benzoic acid is taken internally, it is rejected from the system in the state of hippuric acid, which is then found in the urine.

Hippuric acid dissolves so abundantly in an aqueous solution of sodium phosphate, that this solution loses its alkaline reaction and becomes acid. This reaction may explain the acid character of the recent urine of man and herbivorous animals.

Uramidobenzoic acid, $C_8H_8N_2O_3 = CO<\begin{matrix}NH.C_6H_4.CO.OH\\NH_2\end{matrix}$, is formed by mixing the cold solutions of equivalent quantities of hydrochloride of metamidobenzoic acid and potassium cyanate:

$$C_7H_7NO_2.HCl + CNOK = KCl + C_8H_8N_2O_3;$$

also by fusing urea with metamidobenzoic acid: $C_7H_7NO_2 + CH_4N_2O = NH_3 + C_8H_8N_2O_3$. It crystallises in small needles, containing 1 molecule of water, soluble in hot water and in alcohol. When heated to 200°, it is resolved into H_2O and oxybenzoyl-urea,  $C_8H_6N_2O_2 = CO<\left.\begin{matrix}NH.C_6H_4.CO\\NH\text{———}\end{matrix}\right]$. By boiling with caustic potash, it is resolved into amidobenzoic acid, carbon dioxide, and ammonia.

Uramidobenzoic acid, treated with a mixture of nitric and sulphuric acid, yields three isomeric dinitro-uramidobenzoic acids, which, when boiled with water, are converted into three nitro-amidobenzoic acids, α, β, γ, (p. 523).

Para-uramidobenzoic acid, formed as above from paramidobenzoic acid, crystallises in white shining elongated laminæ, but slightly soluble in water even at the boiling heat. By nitration it yields only one dinitro-paramidobenzoic acid, convertible into one nitro-paramidobenzoic acid.

Diamidobenzoic acid, $C_6H_3(NH_2)_2.CO_2H$.—The six possible modifications of this acid have all been obtained, viz. (CO_2H in 1):

1:2:3, 1:2:4, 1:2:5, 1:2:6, 1:3:4, 1:3:5.

The acids 1:2:3 and 1:3:4 are formed from β and γ nitro-metamidobenzoic acid (p. 523), and yield by distillation ortho-diamidobenzene.

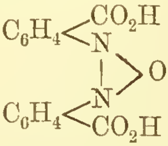
The acids 1:2:6, 1:2:4, and 1:3:5 are formed by reduction of the three corresponding dinitrobenzoic acids (pp. 521, 522), and are converted, by elimination of CO_2, into metadiamidobenzene.

The acid 1:2:5 (or 1:3:6) is formed from α-nitro-metamidobenzoic acid and from the corresponding dinitrobenzoic acid, and is convertible into paradiamidobenzene.

Hence it appears that (1 : 4) diamidobenzene is producible from only *one* diamidobenzoic acid; (1 : 3) diamidobenzene from *three;* and (1 : 2) diamidobenzene from *two* diamidobenzoic acids. This result affords a further confirmation of the structure of the three diamidobenzenes (pp. 424, 451).

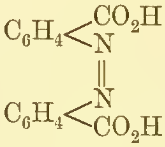
A *triamidobenzoic acid,* $C_6.CO_2H.NH_2.H.NH_2.NH_2.H$, is formed by reduction of (1 : 2 : 4 : 5) dinitramidobenzoic acid. It crystallises in shining needles containing $\frac{1}{2}H_2O$, and is resolved by distillation into CO_2 and triamidobenzene.

Azobenzoic Acids.—The action of sodium-amalgam on the mononitrobenzoic acids (or rather on their sodium-salts) gives rise (as in the case of nitrobenzene, p. 466) to azo-, azoxy-, and hydrazobenzoic acids:



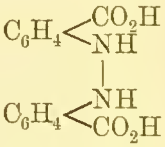
$$\begin{array}{l} C_6H_4<\begin{smallmatrix}CO_2H\\N\end{smallmatrix} \\ \qquad |\;>O \\ C_6H_4<\begin{smallmatrix}N\\CO_2H\end{smallmatrix} \end{array}$$

Azoxybenzoic.



$$\begin{array}{l} C_6H_4<\begin{smallmatrix}CO_2H\\N\end{smallmatrix} \\ \qquad \| \\ C_6H_4<\begin{smallmatrix}N\\CO_2H\end{smallmatrix} \end{array}$$

Azobenzoic.



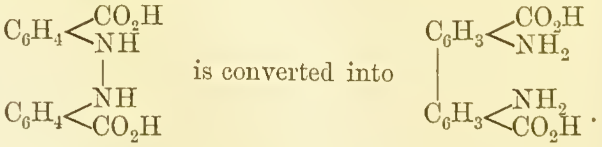
$$\begin{array}{l} C_6H_4<\begin{smallmatrix}CO_2H\\NH\end{smallmatrix} \\ \qquad | \\ C_6H_4<\begin{smallmatrix}NH\\CO_2H\end{smallmatrix} \end{array}$$

Hydrazobenzoic.

Metazobenzoic acid, $C_{14}H_{10}N_2O_4+\frac{1}{2}H_2O$, ($CO_2H$ and N in the relative positions 1, 3), is precipitated by hydrochloric acid from the solution of its sodium salt, as a yellow amorphous powder, very slightly soluble in water, alcohol, and ether; decomposed by distillation. It is bibasic, and forms crystalline yellow salts and ethers. *Parazobenzoic* acid is a flesh-coloured amorphous powder.

Azoxybenzoic acid, $C_{14}H_{10}N_2O_5$ (1 : 3), is formed by boiling an alcoholic solution of metanitrobenzoic acid with solid potash, and is precipitated by hydrochloric acid in yellowish crystalline flocks.—Bibasic.

Hydrazobenzoic acid, $C_{14}H_{12}N_2O_4$, is formed by adding ferrous sulphate to a boiling solution of azobenzoic acid in caustic soda-ley, and is precipitated by hydrochloric acid in yellowish flocks, very slightly soluble in hot alcohol. Its salts in aqueous solution absorb oxygen from the air, whereby they are converted into azobenzoates. By boiling with hydrochloric acid it is converted into an isomeric acid derivable from diphenyl, just as hydrazobenzene is converted into benzidine (p. 467):



$$\begin{array}{l} C_6H_4<\begin{smallmatrix}CO_2H\\NH\end{smallmatrix} \\ \qquad | \\ C_6H_4<\begin{smallmatrix}NH\\CO_2H\end{smallmatrix} \end{array} \text{ is converted into } \begin{array}{l} C_6H_3<\begin{smallmatrix}CO_2H\\NH_2\end{smallmatrix} \\ | \\ C_6H_3<\begin{smallmatrix}NH_2\\CO_2H\end{smallmatrix} \end{array}.$$

The last-mentioned acid is resolved by distillation into CO_2 and benzidine.

Diazo-derivatives of Benzoic Acid.—These compounds are formed from the amidobenzoic acids in the same manner as the diazobenzene-compounds from the amidobenzenes.

Diazobenzoic Nitrate, $C_6H_4 < \begin{matrix} N{=}N.NO_3 \\ CO_2H \end{matrix}$, is formed by the action of nitrous acid on a solution of metamidobenzoic acid in nitric acid. It is sparingly soluble in cold water, and separates therefrom in colourless prisms, which explode violently when heated. Potash added to the aqueous solution throws down a yellow, very unstable mass, probably consisting of free diazobenzoic acid $\left[C_6H_4 < \begin{matrix} CO_2H \\ N{=}N.OH \end{matrix} ? \right]$. The nitrate boiled with water yields meta-oxybenzoic acid. Bromine-water added to the aqueous solution throws down the perbromide, $C_7H_5N_2O_2Br_3$, as an oil which solidifies in yellow prisms, and is resolved by heating with alcohol into nitrogen, bromine, and metabromobenzoic acid.

Diazo-amidobenzoic acid, $C_{14}H_{11}N_3O_4 = C_6H_4 < \begin{matrix} N{=}N{-}NH{-}C_6H_4{-}CO_2H \\ CO_2H \end{matrix}$, is precipitated, on passing nitrous acid into the alcoholic solution of metamidobenzoic acid, as an orange-red crystalline powder, nearly insoluble in water, alcohol, and ether. It is a weak bibasic acid, and its salts in aqueous solution are very unstable. The acid, heated with haloïd acids, yields the corresponding halogen-derivatives of benzoic acid.

Diazo- and diazo-amido-compounds of exactly similar character are obtained from ortho- and para-amidobenzoic acid.

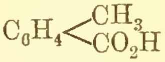
Sulphobenzoic Acids, $C_6H_4 < \begin{matrix} CO_2H \\ SO_3H \end{matrix}$.—When vapour of sulphuric anhydride is passed over dry benzoic acid, and the product is treated with water, or when benzoic acid is heated for a considerable time with fuming sulphuric acid, the chief product formed is *meta*-sulphobenzoic acid, the *para*-acid being also produced in small quantity. The latter is obtained in the pure state by oxidation of para-toluenesulphonic acid (p. 474), or para-sulphocinnamic acid, with chromic acid mixture.

The *meta*-acid is a colourless, crystalline, very deliquescent, strongly acid mass, converted by distillation with PCl_5 into metachlorobenzoyl chloride. It is a very stable bibasic acid: its neutral barium salt is very soluble. The *para*-acid, $C_7H_6SO_5$, crystallises in non-deliquescent needles, melting above 200°, and decomposing even at a lower temperature. Its neutral barium salt, $C_7H_4SO_5Ba + 2H_2O$, crystallises in small, ramified, easily soluble needles.

Chloro- and Bromo-sulphobenzoic acids are obtained by the action of fuming sulphuric acid on the corresponding derivatives of benzoic acid, and by oxidation of chloro- and bromo-toluenesulphonic acids.

Disulphobenzoic acid, $C_6H_4(CO_2H)(SO_3H)_2$, is formed by heating benzoic acid with fuming sulphuric acid and phosphoric anhydride to 250°. Deliquescent acicular prisms. Tribasic. By distillation with potassium cyanide, it yields a dicyanide (m. p. 159)°, convertible into isophthalic acid. An isomeric disulpho-acid is formed by oxidation of toluenedisulphonic acid.

Toluic Acids, $C_8H_8O_2$.—Of these acids there are two metameric modifications, viz.:



$C_6H_4\!<\!\begin{matrix}CH_3\\CO_2H\end{matrix}$

Toluic or methyl-benzoic.

$CH_2\!<\!\begin{matrix}C_6H_5\\CO_2H\end{matrix}$;

Alpha-toluic or phenyl-acetic.

the first admitting of the three isomeric modifications, *o*-, *m*-, *p*-. These three toluic acids are formed by oxidation of the corresponding dimethyl-benzenes (xylenes) with nitric acid diluted with 3 volumes of water; also from the corresponding cyanotoluenes, $C_6H_4(CN).CH_3$, by the action of alcoholic potash, or of strong hydrochloric acid. By oxidation with chromic acid mixture, or potassium permanganate, they are converted into the corresponding phthalic acids, $C_6H_4(CO_2H)_2$.

Orthotoluic acid crystallises in long slender needles melting at 102·5°; is moderately soluble in hot water, and distils easily with aqueous vapour. By oxidation with permanganate it yields phthalic acid, whereas chromic acid mixture oxidises it completely to carbonic acid. Its *calcium salt*, $(C_8H_7O_2)_2Ca + 2H_2O$, and *barium salt*, $(C_8H_7O_2)_2Ba$, form slender needles easily soluble in water.

Metatoluic acid is best obtained from cyanotoluene, or by the action of sodium-amalgam on bromometatoluic acid. It is more soluble in water than its two isomerides, and crystallises from hot water in slender needles, melting at 109°–110°; distils easily with aqueous vapour. Chromic acid mixture oxidises it readily to isophthalic acid. Its *calcium salt*, $(C_8H_7O_2)Ca + 3H_2O$, crystallises from alcohol in needles, easily soluble in water.

Bromometatoluic acid, $C_8H_7BrO_2$, is formed by heating nitroparabromotoluene with alcoholic potassium cyanide to 220°, and saponifying the product with potash.

Paratoluic acid, obtained by oxidation of (1:4) xylene, or of cymene, with dilute nitric acid, crystallises in needles melting at 178°. Its calcium salt, $(C_8H_7O_2)_2Ca + 2H_2O$, forms needles easily soluble in water. Chromic acid mixture oxidises it to terephthalic acid.

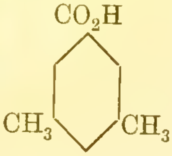
Alpha-toluic or *Phenyl-acetic acid*, $C_6H_5.CH_2.CO_2H$, is formed by boiling benzyl cyanide, $C_6H_5.CH_2.CN$, with alkalis; by heating mandelic acid, $C_6H_5.CH(OH).CO_2H$, with hydriodic acid;

by boiling vulpic acid, $C_{19}H_{14}O_5$ (p. 544), with baryta; and as an ethylic ether, by heating a mixture of bromobenzene and ethyl chloracetate with sodium:

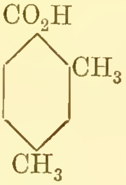
$$C_6H_5Br + CH_2Cl.CO_2C_2H_5 + Na_2 = NaBr + NaCl + C_6H_5.CH_2.CO_2C_2H_5.$$

It crystallises from boiling water in broad thin laminæ, very much like benzoic acid; smells like horse-sweat; melts at 76·5°, and boils at 261°–262°. By distillation with PCl_5 it yields the chloride $C_6H_5.CH_2.COCl$, which passes over as a colourless heavy liquid. By oxidation with chromic acid mixture it yields benzoic acid.

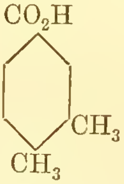
Acids, $C_9H_{10}O_2$. — Of the six possible dimethyl-carbonic acids, $C_6H_3(CH_3)_2.CO_2H$, three are known, viz.:



Mesitylenic.



Xylic.



Paraxylic.

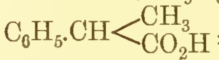
Mesitylenic acid (1:3:5), formed by oxidising mesitylene with dilute nitric acid, crystallises from alcohol in large prisms, from water in needles; melts at 166°, and sublimes without decomposition. Distilled with excess of lime it yields isoxylene. By nitric acid it is further oxidised to trimesic and uvitic acids. Its *barium salt*, $(C_9H_9O_2)_2Ba$, dissolves easily in water, and forms large shining prisms. The *ethylic ether*, $C_9H_9O_2.C_2H_5$, solidifies at 0°, and boils at 241°.

Xylic acid (1:2:4), and Paraxylic acid (1:3:4), are formed, together with bibasic xylidic acid, $C_6H_3(CH_3).(CO_2H)_2$, by oxidising pseudocumene (p. 431) with dilute nitric acid at the boiling heat. At the end of the reaction a crystalline mass separates, and on repeatedly boiling this mass with water, xylic and paraxylic acids pass over, while xylidic acid and nitro-acids remain behind. The xylic and paraxylic acids are separated by the different solubility of their calcium salts, the xylate being the more soluble of the two. Both acids crystallise in prisms, xylic acid melting at 126°, paraxylic acid at 163°. Xylic acid is more soluble in water than paraxylic acid. Both acids dissolve easily in alcohol.

Alphaxylic acid, $C_6H_4(CH_3).CH_2.CO_2H$, is obtained by boiling xylyl chloride with potassium cyanide (whereby xylyl cyanide, C_8H_9CN, is produced), and then with potash. It crystallises in broad needles, having a satiny lustre, easily soluble in water, and boiling at 42°.

Ethyl-benzoic acid, $C_6H_4(C_2H_5).CO_2H$ (1:4), obtained by oxidation of para-diethylbenzene with nitric acid, and from bromethylbenzene by the action of Na and CO_2, crystallises from hot water in slender laminæ melting at 110°, and easily subliming. By oxidation it yields terephthalic acid.

Hydrocinnamic, Phenylpropionic, or Homotoluic acid, $C_6H_5.CH_2.CH_2.CO_2H$, is formed by the action of sodium amalgam, or of very strong hydriodic acid at 100°, on cinnamic acid, $C_6H_5.CH{=}CH.CO_2H$, also by heating chlorethyl-benzene, $C_6H_5.CH_2.CH_2Cl$ (p. 441), with potassium cyanide, and boiling the resulting nitril with potash. It crystallises in slender needles, easily soluble in hot water and in alcohol, melts at 47° and distils without decomposition at 280°. By oxidation it yields benzoic acid. Heated to 160° with bromine it is reconverted into cinnamic acid : $C_9H_{10}O_2 + Br_2 = 2HBr + C_9H_8O_2$.



Hydro-atropic acid, $C_6H_5.CH<\begin{smallmatrix}CH_3\\CO_2H\end{smallmatrix}$, formed by the action of sodium amalgam on atropic acid, is a thick oily liquid.

Acids, $C_{10}H_{12}O_2$.—Durylic acid, $C_0H_2(CH_3)_3.CO_2H$, formed by oxidising durene, $C_6H_2(CH_3)_4$, with dilute nitric acid, crystallises in hard prisms melting at 150°, and is converted by oxidation into cumidic acid.

Cumic acid, $C_6H_4(C_3H_7).CO_2H$ (1:4), is obtained by oxidation of cuminol or cumic aldehyde, $C_{10}H_{12}O$, or by heating this aldehyde with alcoholic potash:

$$\underset{\text{Cuminol.}}{2C_{10}H_{12}O} + KOH = \underset{\substack{\text{Potassium}\\\text{cumate.}}}{C_{10}H_{11}KO_2} + \underset{\substack{\text{Cymyl}\\\text{alcohol.}}}{C_{10}H_{14}O}.$$

It crystallises in needles and laminæ, dissolves easily in hot water and in alcohol, melts at 113°, boils at about 290°. By distillation with lime it yields cumene, C_9H_{12}, and by oxidation with chromic acid it is converted into terephthalic acid.

Alphacymic acid, $C_{11}H_{14}O_2$, probably $C_6H_2(CH_3)_3.CH_2CO_2H$, is formed by the action of caustic alkalis on cymyl cyanide, $C_{10}H_{13}.CN$.

MONATOMIC ACIDS, $C_nH_{2n-10}O_2$.

The acids of this series are unsaturated compounds, related to benzoic acid and its homologues, in the same manner as those of the acrylic series to the fatty acids.

Cinnamic Acid, $C_9H_8O_2 = C_6H_5.CH{=}CH.CO_2H$ (*Phenyl-acrylic acid*).—This acid is produced synthetically:—1. By heating benzoic aldehyde in close vessels with acetyl chloride:

$$C_7H_6O + C_2H_3OCl = HCl + C_0H_8O_2.$$

2. By heating the same aldehyde with acetic anhydride and sodium acetate:

$$2C_7H_6O + C_4H_6O_3 = 2C_0H_8O_2 + H_2O.$$

The mode of action in this case is not well understood, but the presence of the sodium acetate appears to be essential.

3. By treating potassium benzoate with chlorethidene, C_2H_3Cl (produced by the action of carbonyl chloride on acetic aldehyde):

$$C_2H_4O + COCl_2 = HCl + CO_2 + C_2H_3Cl$$

and

$$C_2H_3Cl + C_7H_5O_2K = KCl + C_9H_8O_2.$$

4. By the action of sodium and carbon dioxide on monobromocinnamene:

$$C_6H_5.CH{=\!=}CHBr + CO_2 + Na_2 = NaBr + C_6H_5CH{=\!=}CH.CO_2Na.$$

5. Cinnamic acid is also produced by oxidation of cinnamon-oil (cinnamic aldehyde, C_9H_8O) in air or oxygen, and exists ready formed, together with benzoic acid, and certain oily and resinous substances, in Peru and Tolu balsams—the produce of certain South American *Myroxylums* — being doubtless formed by oxidation of cinnyl alcohol or styrone, $C_9H_{10}O$ (p. 504), likewise contained therein. It is easily prepared by mixing pulverised Tolu balsam with an equal weight of slaked lime, filtering hot, and decomposing the calcium cinnamate which crystallises out on cooling, with hydrochloric acid. The mother-liquid contains calcium benzoate.

Cinnamic acid crystallises from hot water in slender needles, from alcohol in thick prisms. It is inodorous, melts at 133°, and distils almost without decomposition at 290°. It is much less soluble in water than benzoic acid, but dissolves easily in alcohol. It is oxidised by nitric acid to benzoic acid and benzoic aldehyde; by chromic acid chiefly to benzoic acid. By fusion with excess of potash it is resolved into benzoic and acetic acids:

$$C_9H_8O_2 + 2H_2O = C_7H_6O_2 + C_2H_4O_2 + H_2,$$

the decomposition being precisely analogous to that of an acid of the acrylic series into two acids of the fatty series (p. 306). By distillation with lime or baryta, and partly also when distilled alone, it is resolved into carbon dioxide and cinnamene, C_8H_8 (p. 433).

The metallic cinnamates, $C_8H_7MO_2$ (for monatomic metals) are very much like the benzoates.

Ethyl Cinnamate, $C_9H_7O_2.C_2H_5$, obtained by passing gaseous hydrogen chloride into a solution of cinnamic acid in absolute alcohol, is a liquid boiling at 267°.

Benzyl Cinnamate or *Cinnamein*, $C_9H_7O_2.C_7H_7$, is contained in Peru and Tolu balsams, in small quantity also in storax, and may be formed artificially by heating sodium cinnamate with benzyl chloride. It crystallises in shining prisms melting at 39°, distilling without decomposition only under reduced pressure.

Cinnyl Cinnamate or *Styracin*, $C_9H_7O_2.C_9H_9$, occurs, together with cinnamene, in liquid storax (which exudes from *Styrax calamita*, a shrub growing in Greece and Asia Minor), and may be obtained therefrom by distilling the balsam to expel the cinnamene, then boiling it with aqueous sodium carbonate to remove free cinnamic acid, and kneading the spongy residue between the fingers. The styracin then runs out as an oily liquid, and may be obtained in tufts of prisms by crystallisation from alcohol. By distillation with potash it is resolved into cinnyl or styryl alcohol, $C_9H_{10}O$, and cinnamic acid.

Addition-products of Cinnamic Acid.—This acid, like other unsaturated compounds, can take up H_2, HBr, ClOH, &c.; thus it is converted by sodium-amalgam into hydrocinnamic acid, $C_9H_{10}O_2$ (p. 530).

Cinnamic Dibromide, $C_9H_8Br_2O_2 = C_6H_5.CHBr.CHBr.CO_2H$, formed by the action of bromine vapour on cinnamic or on hydrocinnamic acid, crystallises from alcohol in rhombic laminæ, melting, with decomposition, at about 195°. By boiling with water it is resolved into monobromocinnamene and phenylbromolactic acid, $C_6H_5.CHBr.CH(OH).CO_2H$.

This last mentioned acid is also formed by direct addition of BrHO to cinnamic acid, and phenyl-chlorolactic acid in like manner by addition of ClOH. Both these acids are converted, by heating with alcoholic potash, into phenyloxyacrylic or oxycinnamic acid, $C_6H_5.CH{=}C(OH).CO_2H$, which separates from its salts as an oil, solidifying in shining laminæ, and decomposed by heat.

Substitution-products.—Cinnamic dibromide heated with alcoholic potash yields two isomeric monobromocinnamic acids, viz.:

$$\underset{\alpha}{C_6H_5.CH{=}CBr.CO_2H} \qquad \underset{\beta}{C_6H_5.CBr{=}CH.CO_2H}$$

Both are crystalline. The α-acid melts at 130°, and forms salts which crystallise readily; the β-acid melts at 120°, and forms deliquescent salts. α unites with 2 atoms of bromine, and is converted by sodium-amalgam into hydrocinnamic acid; β is converted into α by distillation, or by heating with hydriodic acid.

Two nitrocinnamic acids (*ortho-* and *para-*) are formed by direct nitration, and may be separated by the different solubilities of their ethylic ethers in cold alcohol, the *p*-compound being nearly insoluble. The *o*-compound melts at 232°, the *p*-compound at 265°. Both are converted by chromic acid into the corresponding nitrobenzoic acids.

The following homologues of cinnamic acid (which cannot here be described) are formed by heating benzoic and cumic aldehydes with the sodium salt of a fatty acid, $C_nH_{2n}O_2$, and the corresponding anhydride, $(C_nH_{2n-1}O)_2O$, *e.g.*, phenylcrotonic acid from benzoic aldehyde, sodium propionate, and propionic anhydride—the mode of formation being exactly analogous to that of cinnamic acid from C_7H_6O and $C_4H_6O_3$ (p. 530) :

Acids from Benzoic Aldehyde.		*Acids from Cumic Aldehyde.*	
Phenylcrotonic,	$C_{10}H_{10}O_2$	Cumenyl-acrylic,	$C_{12}H_{14}O_2$
Isophenylcrotonic,	$C_{10}H_{10}O_2$	Cumenyl-crotonic,	$C_{13}H_{16}O_2$
Phenyl-angelic,	$C_{11}H_{12}O_2$	Cumenyl-angelic,	$C_{14}H_{18}O_2$

An Isophenylcrotonic acid is formed by the action of succinic anhydride and sodium succinate on benzoic aldehyde:

$$C_4H_4O_3 + C_7H_6O = CO_2 + C_{10}H_{10}O_2 .$$

Sodium-amalgam converts these acids into acids of the series $C_nH_{2n-8}O_2$; *e.g.*, hydrocumenylacrylic, $C_{12}H_{16}O_2$.[*]

Atropic and **Isatropic Acids,** isomeric with cinnamic acid, are formed simultaneously from tropic acid (p. 538), by boiling with baryta-water or hydrochloric acid: $C_9H_{10}O_3 - H_2O = C_9H_8O_2$.

Atropic acid, the chief product formed when baryta is used, crystallises from hot water in monoclinic plates, slightly soluble in cold water, melting at 106·5°. It is oxidised by chromic acid mixture to benzoic acid; converted by sodium-amalgam into hydroatropic acid (p. 530); and resolved by fusion with potash into alpha-toluic acid, $C_6H_5.CH_2.CO_2H$, and formic acid, whereas cinnamic acid similarly treated yields benzoic and acetic acids; hence it appears that atropic acid is related to cinnamic acid in the same manner as methacrylic to solid crotonic acid (p. 307):

$CH_3—CH{=}CH—CO_2H$ Crotonic.	$CH_2{=}C(CH_3)(CO_2H)$ Methacrylic.
$C_6H_5—CH{=}CH—CO_2H$ Cinnamic.	$CH_2{=}C(C_6H_5)(CO_2H)$ Atropic.

Isatropic acid, probably a polymeric modification, is the chief product obtained by heating tropic acid with hydrochloric acid to 140°. It forms thin laminæ, very slightly soluble in water, melts at 200°; does not unite with nascent hydrogen.

Acids, $C_nH_{2n-12}O_2$;—

Phenyl-propiolic acid, $C_9H_6O_2 = C_6H_5—C{\equiv}C—CO_2H$, is formed: 1. By boiling α-bromocinnamic acid with alcoholic potash. 2. By the action of Na and CO_2 on α-bromocinnamene, $C_6H_5—C_6H_5CH{=}CHBr$. 3. By the action of CO_2 on sodium-acetenylbenzene (p. 434) dissolved in ether:

$$C_6H_5—C{\equiv}CNa + CO_2 = C_6H_5—C{\equiv}C—CO_2Na .$$

It crystallises from hot water in long shining needles; melts and sublimes at 136°-137°; melts under water at 80°. It is oxidised by chromic acid mixture to benzoic acid; converted by sodium-amalgam into hydrocinnamic acid; resolved by heating with water to 120° into CO_2 and phenyl-acetylene, $C_6H_5.C{\equiv}CH$ (p. 434).

Homologous with phenyl-propiolic acid are the following acids formed from cinnamic aldehyde, C_9H_8O, by the action of the anhydrides and sodium salts of fatty acids, viz.:

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[*] Perkin, *Chem. Soc. Jour.* 1877, i. 388.

Cinnamenyl-acrylic acid, ...	$C_{11}H_{10}O_2$
Cinnamenyl-crotonic acid, . . .	$C_{12}H_{12}O_2$
Cinnamenyl-angelic acid, ...	$C_{13}H_{14}O_2$.

MONOBASIC AND DIATOMIC ACIDS.

$$(1.)\ C_nH_{2n-8}O_3 \text{ or } C_nH_{2n-8}\left\{\begin{matrix} OH \\ CO_2H \end{matrix}\right. .$$

These aromatic oxy-acids, like the corresponding acids of the fatty series (the lactic acids), exhibit alcoholic as well as acid characters. In contact with carbonates they give up only the hydrogen-atom of the CO_2H-group in exchange for a metal (forming neutral salts), but when acted upon by strong free bases (caustic alkalis), they likewise exchange the hydrogen of the hydroxyl-group (the alcoholic or phenolic hydrogen) for metals, forming so-called basic salts, *e.g.*, $C_6H_4(ONa)(CO_2Na)$. These, like the metallic derivatives of the phenols, are decomposed by carbonic acid, and converted into neutral salts.

The aromatic oxy-acids are formed from the halogen-derivatives of benzoic acid and its homologues, and from the sulpho-acids, by fusion with alkalis; from the amido-derivatives of the same acids by the action of nitrous acid; and from the phenols by the action of sodium and carbon dioxide.

Oxybenzoic Acids, $C_7H_6O_3 = C_6H_4(OH).CO_2H$.

1. ORTHO-OXYBENZOIC or SALICYLIC ACID (1:2), is formed:

(1.) By heating sodium phenate in a stream of carbon dioxide, phenol then distilling over, while disodium salicylate remains behind:

$$2C_6H_5ONa + CO_2 = C_6H_4ONa.CO_2Na + C_6H_5OH.$$

The reaction takes place even below 100°, but proceeds most quickly between 170° and 180°, and goes on in the same way up to 300°, at which temperature the sodium salicylate begins to decompose. This process is applied to the preparation of salicylic acid on the large scale. Potassium phenate heated in a stream of carbon dioxide is decomposed in the same manner, yielding pure dipotassium salicylate up to 150°; but above that temperature the isomeric paraoxybenzoate is likewise produced, increasing in proportion as the temperature rises, and becoming the sole product at 220°. Monopotassium salicylate is decomposed in the same manner at 220°, yielding a distillate of phenol and a residue of dipotassium paraoxybenzoate:

$$2(C_6H_4(OH).CO_2K) = C_6H_4(OK).CO_2K + C_6H_5OH + CO_2;$$

and the monosodium salt undergoes a similar decomposition, yielding however, not paraoxybenzoate, but salicylate of sodium.

(2.) By oxidation of salicylic aldehyde or of saligenin (p. 507).

(3.) By the action of nitrous acid on (1:2) amidobenzoic (anthanilic) acid:

$$C_6H_4(NH_2).CO_2H + NO.OH = C_6H_4(OH).CO_2H + N_2 + H_2O.$$

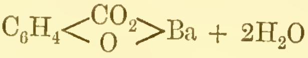
(4.) By fusing (1:2) chloro- or bromobenzoic acid, or (1:2) toluenesulphonic acid with alkalis.

(5.) Together with acetic acid, by heating coumaric acid with potassium hydroxide:

$$C_9H_8O_3 + 2H_2O = C_7H_6O_3 + C_2H_4O_2 + H_2.$$

Salicylic acid occurs in the free state in the flowers of meadow-sweet (*Spiræa ulmaria*), and as a methylic ether in oil of winter-green (*Gaultheria procumbens*), from which it may be obtained by distillation with potash.

Salicylic acid crystallises from its alcoholic solution by spontaneous evaporation in large monoclinic prisms. It requires about 1800 parts of cold water to dissolve it, but is much more soluble in hot water and in alcohol. Its aqueous solution imparts a deep violet colour to ferric salts. It melts at 155°–156°, gives off phenol at a higher temperature, and when heated with pounded glass or quicklime, is completely resolved into carbon dioxide and phenol. It is distinguished from both its isomerides by its behaviour with ferric salts, its very slight solubility in water, and its lower melting point. It is a very powerful antiseptic.

Basic Barium salicylate,  $C_6H_4{<}\substack{CO_2\\O}{>}Ba + 2H_2O$, separates in springly soluble laminæ on boiling salicylic acid with baryta-water, both the hydroxylic hydrogen-atoms being replaced by barium. The *basic calcium salt* is formed in a similar manner, and separates as an insoluble powder. This reaction affords another distinction between salicylic acid and its isomerides.

Halogen-derivatives of Salicylic acid are easily formed by the direct action of bromine and chlorine; also of iodine, in presence of HgO or IO_3H. By nitration salicylic acid yields three nitro-acids.

Salicylic chloride, $C_6H_4Cl.CO.Cl$, formed by the action of PCl_5 on the acid, is an oil which boils at 240°, and is converted by hot water into *o*-chlorobenzoic acid.

Salicylic anhydride or Salicylide, $C_6H_4{<}\substack{CO\\O}{>}$, formed by the action of PCl_3O on salicylic acid, crystallises in shining needles, dissolves sparingly in water, and is reconverted by alkalis into salicylic acid.

Salicylamide, $C_6H_4(OH).CO.NH_2$, formed by heating ammonium salicylate, or by the action of ammonia on salicylic ethers forms sparingly soluble laminæ melting at 132°.

Salicylic ethers are formed by passing gaseous hydrogen chloride into the solutions of salicylic acid in the corresponding alcohols. The *monomethylic ether*, $C_6H_4(OH).CO_2CH_3$, is the chief constituent of winter-green oil. It is a fragrant liquid of specific gravity 1·197 at 0°, boiling at 224°, coloured violet by ferric chloride. The *monethylic ether* boils at 221°.

The *dimethylic ether*, $C_6H_4(OCH_3).CO_2CH_3$, an oil boiling at 240°, is formed by heating the monomethylic ether with alcoholic potash and methyl oxide:

$$C_6H_4(OK).CO_2CH_3 + CH_3I = KI + C_6H_4(OCH_3).CO_2CH_3 .$$

This ether, saponified with potash, yields methyl alcohol and methylsalicylic acid, $C_6H_4(OCH_3).CO_2H$, which forms large tabular crystals, melting at 98°, easily soluble in hot water and alcohol, resolved at 200° into CO_2 and anisol, $C_6H_5.OCH_3$.

Diethyl salicylate and *Ethylsalicylic acid* are formed in like manner; the latter melts at 19·5°, and is resolved at 300° into CO_2, and phenetol, $C_6H_5.O.C_2H_5$.

Acetyl-salicylic acid, $C_6H_4(O.C_2H_3O).CO_2H$, formed by the action of acetyl chloride on salicylic acid, crystallises in slender needles.

META-OXYBENZOIC ACID, $C_6H_4(OH).CO_2H$ (1:3), ordinary oxybenzoic acid, is formed by the action of nitrous acid on metamidobenzoic acid, and by fusing metabromo-, iodo-, or sulpho-benzoic acid with potash. It is sparingly soluble in cold water and alcohol, easily in the same liquids when hot, and separates on cooling as a crystalline powder. It melts at 200°, sublimes undecomposed, and is altogether more stable than either of its isomerides, being resolved into CO_2 and phenol only by distillation with lime. It is not coloured by ferric chloride. Its *ethylic ether*, $C_6H_4(OH).CO_2C_2H_5$, crystallises in plates, dissolves in hot water, melts at 72°, and boils at 280°. The *dimethylic ether*, $C_6H_4(OCH_3).CO_2.CH_3$, is formed by heating the acid with CH_3I and KOH to 140°, and converted by boiling with potash into *methyloxybenzoic acid*, $C_6H_4(OCH_3).CO_2H$, which crystallises in long needles, dissolves easily in hot water, melts at 100°, and sublimes undecomposed.

PARA-OXYBENZOIC ACID, $C_6H_4(OH).CO_2H$ (1:4), is formed as above mentioned, by heating potassium phenate in a stream of carbon dioxide; also from (1:4) chloro-, bromo-, iodo-, and sulphobenzoic acid, and from various resins, by fusion with potassium hydroxide; by the action of nitrous acid on paramidobenzoic acid; and by heating anisic (methyl-paraoxybenzoic) acid with strong hydriodic acid: $C_7H_5(CH_3)O_3 + HI = CH_3I + C_7H_6O_3$. It is more soluble in cold water than metaoxybenzoic or salicylic acid, dissolving in 126 parts of water at 15°: from a hot solution it crystallises in small distinct monoclinic prisms, containing 1 mol. H_2O. Its solution forms, with ferric chloride, a yellow precipitate insoluble in excess, without violet coloration. In the anhydrous state it melts at 210°, with partial resolution into CO_2 and phenol. Its basic barium-salt, $C_6H_4\!<\!\genfrac{}{}{0pt}{}{O}{CO_2}\!>\!Ba$, is insoluble, and affords the means of separating paraoxybenzoic acid from the meta-acid.

Monomethylic paraoxybenzoate forms large tabular crystals, melts at 17°, and boils at 283°. The *ethylic ether* melts at 113°, and boils at about 297°.

Methyl-paraoxybenzoic and Ethyl-paraoxybenzoic acids are prepared in the same manner as the ortho- and meta-compounds.

Methyl-paraoxybenzoic or *Anisic acid*, $C_6H_4(OCH_3).CO_2H$, is also produced by oxidation of anisaldehyde and anethol (p. 504)—or the crude oils of anise, fennel, and tarragon, which contain anethol—with nitric acid or chromic acid mixture. The anethol is first converted into anisaldehyde :

$$\underset{\text{Anethol.}}{C_{10}H_{12}O} + O_6 = \underset{\text{Anis-aldehyde.}}{C_8H_8O_2} + \underset{\text{Oxalic acid.}}{C_2H_2O_4} + H_2O,$$

and the aldehyde is afterwards oxidised to anisic acid. Anisic acid is also produced by oxidation of methyl-paracresol, $C_6H_4(OCH_3).CH_3$.

Anisic acid crystallises from hot water in long needles, from alcohol in rhombic prisms; melts at 183°; sublimes and boils without decomposition at 283°. By heating with lime or baryta it is resolved into CO_2 and anisol, $C_6H_5.O.CH_3$. Heated with HCl or HI, it yields paraoxybenzoic acid. Its salts are easily soluble in water, and crystallise well.

With the halogens and with nitric acid, anisic acid readily yields substitution-products, which are converted by distillation with baryta into substituted anisols. By the successive action of fuming nitric acid and ammonia, anisic acid is converted into chrysanisic acid $C_6H_2(NO_2)_2(NH_2).CO_2H$ (p. 523).

Acids, $C_8H_8O_3 = C_7H_6{<}^{OH}_{CO_2H}$.

1. Cresotic, or Oxytoluic Acids, $C_6H_3(CH_3){<}^{OH}_{CO_2H}$.—Three cresotic acids are formed by the action of Na and CO_2 on the three isomeric cresols (p. 487) :

$$C_6H_4(CH_3)OH + CO_2 = C_6H_3(CH_3)(OH)(CO_2H).$$

They crystallise in needles, dissolve in hot water, and are coloured violet by ferric chloride. The acid from *o*-cresol melts at 163°–164°; that from *m*-cresol at 114°; that from *p*-cresol at 153°.

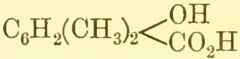
A fourth oxytoluic acid is obtained from sulphotoluic acid (from camphor-thiocymene) by fusion with potash ; it melts at 203°, and is not coloured by ferric chloride.

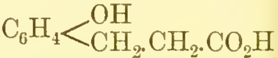
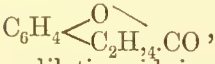
2. Mandelic or Phenylglycollic Acid, $C_6H_5.CH{<}^{OH}_{CO_2.H}$, is formed by boiling bitter almond oil for 30–36 hours with hydrocyanic and hydrochloric acids :

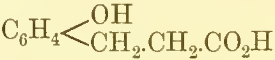
$$C_6H_5.CHO + CNH + 2H_2O = NH_3 + C_6H_5.CHOH.CO_2H;$$

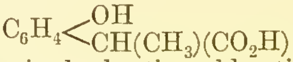
also by heating amygdalin (see GLUCOSIDES) with hydrochloric acid. It crystallises in prisms or tables, easily soluble in water, alcohol, and ether, melting at 115°. By oxidising agents it is converted into benzoic acid; by hydriodic acid into alphatoluic (phenylacetic) acid. With HBr it yields *phenylbromacetic* acid, $C_6H_5.CHBr.CO_2H$, and with HCl the corresponding chlorinated acid.

Acids, $C_9H_{10}O_3$.

1. OXYMESITYLENIC ACID,  $C_6H_2(CH_3)_2{<}\begin{matrix}OH\\CO_2H\end{matrix}$, formed by heating mesitylenesulphonic acid with potash to 240°–250°, crystallises from alcohol in silky needles, melts at 176°, and sublimes in long flat needles. Its solutions and those of its salts are coloured dark blue by ferric chloride.

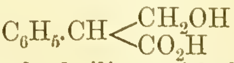
2. HYDROCOUMARIC OR MELILOTIC ACID,  $C_6H_4{<}\begin{matrix}OH\\CH_2.CH_2.CO_2H\end{matrix}$ (1 : 2), occurs in the yellow mellilot, and is formed by the action of sodium on coumarin (p. 540) and coumaric acid: $C_9H_6O_2$ (coumarin) $+H_2O+H_2=C_9H_{10}O_3$. It crystallises in long needles melting at 82°. Its solution is coloured bluish by ferric chloride. By distillation it is converted into the anhydride, $C_9H_8O_2=$  $C_6H_4{<}\begin{matrix}O\diagdown\\C_2H_4.CO\end{matrix}$, which melts at 25°. By fusion with potash melilotic acid, is resolved into acetic and salicylic acid, and is therefore an ortho-diderivative of benzene.

3. HYDROPARACOUMARIC ACID,  $C_6H_4{<}\begin{matrix}OH\\CH_2.CH_2.CO_2H\end{matrix}$ (1 : 4), is produced by the action of sodium-amalgam on paracoumaric acid, and of nitrous acid on para-amidocinnamic acid. It forms small monoclinic crystals, easily soluble in water, alcohol, and ether; melting at 125°. By fusion with potash it yields para-oxybenzoic acid.

4. PHLORETIC ACID,  $C_6H_4{<}\begin{matrix}OH\\CH(CH_3)(CO_2H)\end{matrix}$ (1 : 4), is formed, together with phloroglucin, by heating phloretin with potash-ley:

$$C_{15}H_{14}O_5 + H_2O = C_9H_{10}O_3 + C_6H_6O_3;$$

also by the action of sodium and CO_2 on phlorol, C_8H_9OH (p. 489). It crystallises in long prisms, easily soluble in hot water, melting at 129°. Ferric chloride colours its solution green. By heating with baryta it is resolved into CO_2 and phlorol; by fusion with potash into acetic and paroxybenzoic acids. *Methylphloretic acid* is converted by oxidation into anisic acid.

5. TROPIC ACID,  $C_6H_5.CH{<}\begin{matrix}CH_2OH\\CO_2H\end{matrix}$, *Phenyl-hydracrylic acid,* formed from atropine by boiling with hydrochloric acid or with baryta-water, crystallises in slender prisms melting at 117°. By long boiling with baryta it is converted into atropic and isatropic

acids (p. 533), which by oxidation yield benzoic acid. Tropic acid is therefore a monoderivative of benzene.

6. Phenyl-lactic Acid, $C_6H_5.CH_2.CH{<}^{OH}_{CO_2H}$, Phenyl-chloro-lactic acid, $C_6H_5.CHCl.CH(OH)(CO_2H)$, formed by addition of ClOH to cinnamic acid, $C_6H_5.CH{=}CH.CO_2H$, and phenyl-bromo-lactic acid, formed by boiling cinnamic dibromide, $C_6H_5.CHBr.CHBr.CO_2H$, with water (p. 532), are both converted by sodium amalgam into phenyl-lactic acid. This acid crystallises in concentric groups of needles, very soluble in hot water, melting at 94°. At 180° it decomposes into water and cinnamic acid. When quickly heated it yields cinnamene:

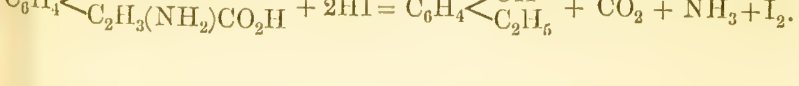
$$C_6H_5.CH_2.CH(OH)(CO_2H) = CO_2 + H_2O + C_6H_5.CH{=}CH_2.$$

Heated with concentrated haloïd acids it exchanges its hydroxyl-group for halogen elements, yielding substituted phenyl-propionic acids, *e.g.*, $C_6H_5.CH_2.CHBr.CO_2H$ (p. 530).

Tyrosine, $C_9H_{11}NO_3$, probably $C_6H_4{<}^{OH}_{C_2H_3(NH_2).CO_2H}$, *Paraoxyphenyl-amidopropionic* or *Amido-hydroparacoumaric acid*, is a compound nearly related to phloretic or hydroparacoumaric acid. It is produced, together with leucine, aspartic acid, and glutamic acid by boiling various animal substances, as albuminoids, horn, hair, &c., with hydrochloric or sulphuric acid, or by fusing them with potash. It sometimes occurs ready-formed in the liver, spleen, and pancreas; also in old cheese (τυρος). It is best prepared by boiling horn-shavings with 2 parts of sulphuric acid diluted with 4 parts of water for about 20 hours, renewing the water as it evaporates. The solution is then saturated with milk of lime, and the tyrosine is precipitated from the concentrated filtrate by acetic acid.

Tyrosine is insoluble in ether, slightly soluble in cold water and in alcohol, dissolves in 150 parts of hot water, and crystallises therefrom in slender needles. It dissolves easily in hydrochloric acid, forming the salt $C_9H_{11}NO_3.HCl$, which crystallises in needles. The aqueous solution of tyrosine boiled with mercuric nitrate yields a yellowish precipitate, which, when boiled with dilute yellow nitric acid, becomes dark red; this is a very delicate test for tyrosine. With chlorine and bromine tyrosine yields chlor- and bromanil, $C_6Cl_4O_2$ and $C_6Br_4O_2$; with nitric acid it yields substitution-products. Sulphuric acid dissolves it, forming sulpho-acids whose salts are coloured violet by ferric chloride.

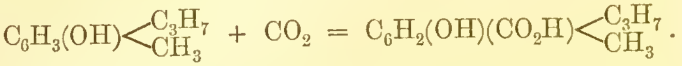
Tyrosine fused with potash is resolved into acetic acid, ammonia, and para-oxybenzoic acid. Heated to 140° with hydriodic acid, it yields phlorol (p. 489), together with CO_2 and NH_3:



$$C_6H_4{<}^{OH}_{C_2H_3(NH_2)CO_2H} + 2HI = C_6H_4{<}^{OH}_{C_2H_5} + CO_2 + NH_3 + I_2.$$

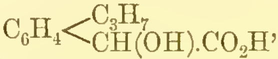
These reactions show that tyrosine is a para-derivative of benzene, containing the NH_2-group in the lateral chain.

Acids, $C_{11}H_{14}O_3$.—Two isomeric acids, thymotic and carvacrotic, are formed by the action of sodium and CO_2 on thymol and carvacrol (p. 489):

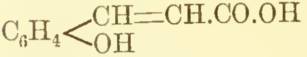


$$C_6H_3(OH)<\begin{matrix}C_3H_7\\CH_3\end{matrix} + CO_2 = C_6H_2(OH)(CO_2H)<\begin{matrix}C_3H_7\\CH_3\end{matrix}.$$

Thymotic acid forms long needles, very slightly soluble in cold water; melts at 120°, and sublimes. Carvacrotic acid sublimes in flat needles, melting at 134°. Both are coloured a fine blue by ferric chloride.

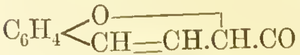
Phenylpropyl-glycollic acid,  $C_6H_4<\begin{matrix}C_3H_7\\CH(OH).CO_2H\end{matrix}$, formed by the action of hydrochloric and hydrocyanic acids on cuminol, crystallises in small needles, moderately soluble in cold water, very soluble in alcohol and ether, melting at 158°.

(2.) UNSATURATED ACIDS, $C_nH_{2n-10}O_3$.

Coumaric and **Paracoumaric Acids**, $C_9H_8O_3$ =  $C_6H_4<\begin{matrix}CH{=}CH.CO.OH\\OH\end{matrix}$, the only known acids of this series, have the composition of oxycinnamic or oxyphenyl-acrylic acid.

Paracoumaric acid (1:4), produced by boiling an aqueous solution of aloes with sulphuric acid, crystallises in colourless, shining, brittle needles, easily soluble in hot water and in alcohol, melting at 170°–180°. By nascent hydrogen it is converted into hydroparacoumaric acid; by fusion with potash, into paraoxybenzoic acid.

Coumaric acid (1:2) occurs, together with melilotic acid (p. 538), in the yellow melilot, and in Faham leaves, and is most easily prepared from coumarin, its anhydride, by boiling with potash. It crystallises in colourless shining prisms, easily soluble in hot water and alcohol, melting at 195°. The solutions of its alkali-salts exhibit a bright green fluorescence. By nascent hydrogen it is converted into melilotic acid; by fusion with potash into salicylic and acetic acids.

Coumarin, $C_9H_6O_2$, or Coumaric anhydride,  $C_6H_4<\begin{matrix}O\text{———————}\rceil\\CH{=}CH.CH.CO\end{matrix}$, is the odoriferous principle of the Tonka bean (*Dipteryx odorata*), and of several other plants, as *Melilotus officinalis*, *Asperula odorata*, and *Anthoxanthum odoratum*. It may be extracted from these plants by alcohol, and crystallises in slender, shining, colourless needles, melting at 67°, boiling between 290° and

291°, and distilling without decomposition at a higher temperature. It has a fragrant odour and burning taste; is very slightly soluble in cold water, more soluble in hot water and in alcohol. It dissolves in potash-ley, and is converted by long boiling therewith into coumaric acid. Sodium-amalgam converts it into melilotic acid.

Coumarin is formed artificially by dehydration of acetosalicylal (isomeric with coumaric acid) in the manner already described (action of acetic anhydride on sodium-salicylal, p. 512):

$$C_7H_5(C_2H_3O)O_2 - H_2O = C_9H_6O_2.$$

By acting on sodium-salicylal in like manner with butyric and valeric anydrides, homologues of coumarin are obtained, viz., butyric coumarin, $C_{11}H_{10}O_2$, and valeric coumarin, $C_{12}H_{12}O_2$. Both crystallise in prisms, the former melting at 71°, and boiling at 297°; the latter melting at 54°, and distilling with partial decomposition at 300°.

MONOBASIC AND TRIATOMIC ACIDS—DIOXYACIDS.

(1.) **Dioxybenzoic Acids,** $C_7H_6O_4 = C_6H_3\left\{\begin{matrix}(OH)_2\\CO_2H\end{matrix}\right.$.—Of six possible isomerides included in this formula, four are known, but the orientation of their lateral chains is not yet completely established.*

Two dioxybenzoic acids are obtained by fusing the two disulphobenzoic acids (p. 527) with potassium hydroxide. One of these dioxy-acids forms crystals containing $1\frac{1}{2}H_2O$, melts with decomposition at about 220°, and is not coloured by ferric chloride. The other, prepared also from toluenedisulphonic acid, forms hydrated crystals melting at 194°, and is coloured dark red by ferric chloride.

Oxysalicylic Acid, $C_6H_3(OH)_2.CO_2H$ (probably 1 : 2 : 3, CO_2H in 1) is formed by boiling a solution of iodosalicylic acid, $C_7H_5IO_3$, with potash. It crystallises in shining needles, soluble in water, alcohol, and ether. The aqueous solution, mixed with ferric chloride, acquires a deep blue colour, changing to red and then brown on addition of ammonia or sodium carbonate. The crystallised acid melts at 196°–197°, and is resolved at a higher temperature into CO_2 and hydroquinone (together with pyrocatechin). The oxysalicylates are very unstable.

Protocatechuic Acid, $C_6H_3(OH)_2.CO_2H$ (probably 1 : 3 : 4, CO_2H in 1); also called *Carbohydroquinonic acid.*—This acid is produced by the action of melting potash on its aldehyde, and on iodoparaoxybenzoic, bromanisic, cresolsulphonic and eugenic acids, catechin, and many other tri-derivatives of benzene; also on numerous resins, as benzoïn, myrrh, dragon's blood, assafœtida, &c.,

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* See Watts's Dictionary of Chemistry, 2nd Supplement, p. 432.

its formation from these resins being usually accompanied by that of paraoxybenzoic acid. It is also formed by the action of bromine on aqueous quinic acid, and by fusing that acid with potash. It is most easily prepared by adding 1 part of East Indian kino to 3 parts of fused sodium hydroxide, dissolving the melt in water, acidulating, and agitating with ether.

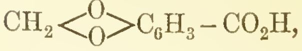
Protocatechuic acid crystallises from water in shining needles or laminæ containing 1 mol. H_2O. It dissolves easily in hot water, in alcohol, and in ether, and in 40–50 parts of cold water; melts at 199°, and decomposes at a higher temperature into CO_2 and pyrocatechin (together with hydroquinone). Ferric chloride colours the solution green, changing, on addition of very dilute sodium carbonate, to blue, and afterwards to red. It reduces silver nitrate, but not an alkaline cupric solution.

Methyl-protocatechuic or *Vanillic acid*, $C_8H_8O_4 = C_6H_3(OH)(OCH_3).CO_2H$, is formed by oxidation of vanillin (p. 512), when that substance, in the moist state, is left exposed to the air, and by oxidation of coniferin, $C_{16}H_{22}O_8$ (see GLUCOSIDES), with potassium permanganate. It crystallises in shining white needles, melting at 211°–212°; sublimable; sparingly soluble in cold water, easily in hot water and in alcohol; decomposed by hydrochloric acid at 150°–160° into methyl chloride and protocatechuic acid. Its calcium salt distilled with lime yields pure guaiacol (p. 491).

An isomeric methyl-protocatechuic acid is formed by heating protocatechuic acid with potassium hydroxide and methyl iodide, also by heating hemipinic acid with strong hydrochloric acid at 100°. It crystallises in slender needles, less soluble than the preceding, and melting at 251°.

Dimethyl-protocatechuic or *Veratric acid*, $C_9H_{10}O_4 = C_6H_3(OCH_3)_2.CO_2H$, is contained in sabadilla seeds (from *Veratrum Sabadilla*), and is formed by heating protocatechuic or methyl-protocatechuic acid with KHO, methyl iodide and methyl alcohol to 140°, and boiling the product with soda-ley; also by oxidation of dimethyl-protocatechuic aldehyde (p. 512), methyl-cresol (p. 408), and methyl-eugenol (p. 505), with permanganate. Colourless needles melting at 179·5°; slightly soluble in cold water, more easily in hot water, still more in alcohol. Heated to 140°–150° with dilute hydrochloric acid, it yields a mixture of two monomethyl-protocatechuic acids. Heated with lime or baryta, it is resolved into CO_2 and dimethyl-pyrocatechin.

In like manner are obtained:—*Diethyl-protocatechuic acid* (needles, m. p. 149°), and *Ethyl-methyl-protocatechuic* or *Ethyl-vanillic acid* (needles slightly soluble in hot water; m.p. 190°).

Methene-protocatechuic or *Piperonylic acid*, $C_8H_6O_4$ =  $CH_2{<}^{O}_{O}{>}C_6H_3-CO_2H$, is formed by oxidation of its aldehyde piperonal $C_8H_6O_3$ (p. 513), with permanganate, and by heating protocatechuic acid with KOH and CH_2I_2.—Colourless needles, m.p. 228°, sublimable without decomposition, insoluble in cold water, slightly soluble in boiling water and cold alcohol, easily in hot alcohol. Decomposed by heating to 170° with dilute hydrochloric acid into protocatechuic acid and free carbon; by heating with water to 200°–210°, into pyrocatechin, CO_2, and carbon.

Ethene-protocatechuic acid, $C_9H_8O_4$, obtained by heating protocatechuic acid with KOH, $C_2H_4Br_2$, and a little water to 100°, forms shining prisms melting at 133·5°

Acids, $C_8H_8O_4 = C_6H_2(CH_3)\left\{\begin{matrix}(OH)_2\\ CO_2H\end{matrix}\right.$.

Orsellinic Acid is formed by boiling orsellic or lecanoric acid with lime-water: $C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4$; also by boiling its erythritic ether (erythrin or erythric acid) with water or baryta-water:

$$\underset{\text{Erythrin.}}{C_{20}H_{22}O_{10}} + H_2O = \underset{\text{Orsellinic acid.}}{C_8H_8O_4} + \underset{\text{Picroerythrin.}}{C_{12}H_{16}O_7};$$

Orsellinic acid crystallises in prisms easily soluble in water, coloured violet by ferric chloride. It melts at 176°, decomposing at the same time into CO_2 and orcin, $C_7H_8O_2$ (p. 496).

Ethyl Orsellinate, $C_6H_2(CH_3)(OH)_2.CO_2.C_2H_5$, is obtained by boiling orsellenic acid, or *Roccella tinctoria*, with alcohol. It crystallises in lustrous plates easily soluble in boiling water, alcohol, and ether.

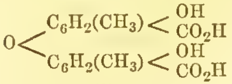
Erythritic Orsellinate, Erythrin or Erythric acid, $C_{20}H_{22}O_{10} = 2C_8H_8O_4 + C_4H_{10}O_4$ (erythrite) $- 2H_2O$, is contained in *Roccella fusiformis*, and extracted by boiling with milk of lime. It forms crystals containing $\frac{3}{2}H_2O$, slightly soluble in hot water, coloured red by ammonia in contact with air, and is resolved by boiling with baryta-water into orsellinic acid and picroerythrin (see above).

Picroerythrin, $C_{12}H_{16}O_7$, forms crystals containing 1 mol. H_2O, soluble in alcohol and ether, and is resolved by further boiling with baryta-water into erythrite, orcin, and carbon dioxide:

$$C_{12}H_{16}O_7 + H_2O = C_4H_{10}O_4 + C_7H_8O_2 + CO_2.$$

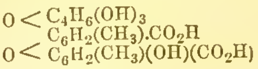
Orsellic, Lecanoric, or *Diorsellinic acid*, $C_{16}H_{14}O_7 = 2C_8H_8O_4 - H_2O$, occurs in several lichens belonging to the genera *Roccella*, *Lecanora*, and *Variolaria*, and is extracted by digestion with ether or with milk of lime, and precipitation by hydrochloric acid. It crystallises from alcohol or ether in colourless prisms containing $C_{16}H_{14}O_7 + H_2O$, nearly insoluble in water. By boiling with lime or baryta-water it is converted, first into orsellinic acid, afterwards into CO_2 and orcin. Its alcoholic solution yields, on boiling, crystalline ethyl orsellinate.

The three compounds last described may be represented by the following structural formulæ:



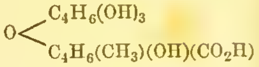
$$O<\begin{array}{l}C_6H_2(CH_3)<\begin{array}{l}OH\\CO_2H\end{array}\\C_6H_2(CH_3)<\begin{array}{l}OH\\CO_2H\end{array}\end{array}$$

Orsellic or
Diorsellinic acid.



$$\begin{array}{l}O<\begin{array}{l}C_4H_6(OH)_3\\C_6H_2(CH_3).CO_2H\end{array}\\O<C_6H_2(CH_3)(OH)(CO_2H)\end{array}$$

Erythrin.



$$O<\begin{array}{l}C_4H_6(OH)_3\\C_4H_6(CH_3)(OH)(CO_2H)\end{array}$$

Picroerythrin.

According to Stenhouse,* the South African variety of *Roccella tinctoria* contains an acid, $C_{34}H_{32}O_{15}$, called β-orsellic acid, closely resembling orsellic acid in properties and composition, and yielding orsellinic acid when boiled with baryta-water, together with roccellinin, $C_{18}H_{16}O_7$, a substance forming hair-like crystals of a silvery lustre: $C_{34}H_{32}O_{15} = 2C_8H_8O_4 + C_{18}H_{16}O_7$. Roccellinin is not attacked by boiling with potash or baryta. It dissolves in ammonia and the fixed alkalis, forming solutions which are not coloured by exposure to the air.

The following acids of unknown structure are also obtained from lichens:

Vulpic acid, $C_{19}H_{14}O_5$, occurs in *Cetraria vulpina*, from which it may be extracted by chloroform or lime-water. It forms large yellow prisms, slightly soluble in water and in ether, melts at 110°, sublimes without decomposition, and is resolved by boiling with baryta-water into alphatoluic acid, methyl alcohol, and oxalic acid.

Usnic acid, $C_{18}H_{18}O_7$, from lichens of the genera *Usnea* and *Evernia*, crystallises in shining yellow laminæ, insoluble in water, slightly soluble in alcohol and ether, melting at 195°–197°. Its alkali-salts, when exposed to the air, turn red and afterwards black. A modification, called Beta-usnic acid, from *Cladonia rangiferina*, melts at 175°, and yields by distillation, beta-orcin (p. 497).

Cetraric acid, $C_{18}H_{16}O_8$, and Lichenic acid, $C_{14}H_{24}O_3$, from Iceland moss (*Cetraria islandica*), are crystalline, and easily soluble in alcohol and ether.

Acids, $C_9H_{10}O_4 = C_8H_7(OH)_2.CO_2H$:

Everninic Acid is formed from evernic acid, $C_{17}H_{16}O_7$ (a constituent of *Evernia Prunastri*), by boiling with baryta:

$$C_{17}H_{16}O_7 + H_2O = C_9H_{10}O_4 + C_8H_8O_4.$$

It crystallises from hot water in needles, melts at 157°, and is coloured violet by ferric chloride.

Umbellic Acid is formed by the action of sodium-amalgam on umbelliferone: $C_9H_6O_3 + H_2O + H_2 = C_9H_{10}O_4$. It crystallises in colourless needles, melting at 125°, slightly soluble in water, easily in alcohol and ether. With ferric chloride it produces a green colour, turning red on addition of sodium carbonate. Fused with potash it yields resorcin.

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* Phil. Trans. 1848, 69; Liebig's Annalen, lxviii. 59.

Umbelliferone, $C_9H_6O_3$, a compound analogous to coumarin (p. 540), occurs in the bark of *Daphne Mezereum*, and is produced by distillation of galbanum, assafœtida, and other resins of umbelliferous plants. It crystallises from hot water in rhombic prisms, slightly soluble in cold water, easily in hot water and in alcohol; its aqueous solution appears blue by reflected light. It melts at 240°, and sublimes without decomposition; yields resorcin by fusion with potash, and is converted by sodium-amalgam into umbellic acid, just as coumarin is converted into hydrocoumaric acid.

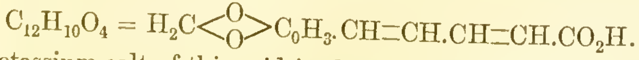
Hydrocaffeic Acid, $C_6H_3(OH)_2—CH_2—CH_2—CO_2H$, formed by the action of sodium-amalgam on caffeic acid, forms crystals easily soluble in water, and is coloured dark-green by ferric chloride.

The following unsaturated acids belong to the triatomic and monobasic division.

Caffeic Acid, $C_9H_8O_4 = C_6H_3(OH)_2—CH=CH—CO_2H$, formed by boiling caffetannic acid (p. 548) with potash, crystallises in yellowish prisms, very soluble in hot water and alcohol. The aqueous solution reduces silver nitrate when heated. Ferric chloride colours it green, changing to dark red on addition of sodium carbonate. By fusion with potash caffeic acid is resolved into protocatechuic and acetic acids. By dry distillation it yields pyrocatechin. Sodium-amalgam converts it into hydrocaffeic acid.

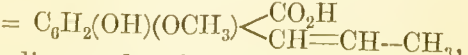
Ferulic Acid, $C_{10}H_{10}O_4 = C_6H_3(OH)_2—C_3H_4—CO_2H$, occurs in assafœtida, and may separated from the alcoholic extract of that substance by precipitating with lead acetate, and decomposing the precipitate with sulphuric acid. It dissolves easily in hot water and alcohol, and crystallises in four-sided needles. Its aqueous solution is coloured yellow-brown by ferric chloride. By fusion with potash it is resolved into protocatechuic and acetic acids.

Piperic Acid,



$$C_{12}H_{10}O_4 = H_2C{<}{\scriptstyle O \atop \scriptstyle O}{>}C_0H_3.CH{=}CH.CH{=}CH.CO_2H.$$

The potassium salt of this acid is obtained by boiling piperine (*q. v.*) with alcoholic potash, and separates in shining prisms. The free acid crystallises in slender needles melting at 216°–217°. It forms sparingly soluble salts containing 1 equivalent of base. It unites with 4 atoms of bromine, and is resolved by fusion with potash into acetic, oxalic, and protocatechuic acids. By oxidation with permanganate solution it yields piperonal (p. 513).



Eugetic Acid, $C_{11}H_{12}O_4 = C_6H_2(OH)(OCH_3){<}{CO_2H \atop CH{=}CH{-}{-}CH_3}$, is formed by the action of sodium and carbon dioxide on eugenol, $C_{10}H_{12}O_2$ (p. 505). It crystallises in thin prisms, slightly soluble in water, melts at 124°, and is resolved at a higher temperature into CO_2 and eugenol. Ferric chloride colours its solution dark brown.

MONOBASIC AND TETRATOMIC ACIDS.

Gallic Acid, $C_7H_6O_5 = C_6H_2(OH)_3.CO_2H$ — *Trioxybenzoic acid, Dioxysalicylic acid.*—This acid occurs in nut-galls (excrescences formed on the leaves and leaf-stalks of the dyer's oak (*Quercus infectoria*), also in sumach, hellebore root, divi-divi (the fruit of *Cisalpina coriaria*), in tea, in pomegranate root, and in many other plants. It is produced artificially by heating di-iodosalicylic acid to 140°–150°, with excess of an alkaline carbonate; and from bromodioxybenzoic acid and bromoprotocatechuic acid (p. 541) by fusion with potash: hence its structure is either 1:2:3:4 or 1:2:4:5 (CO_2H in 1). It is most conveniently prepared by boiling gallotanic acid with acids or alkalis: $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$.

Gallic acid crystallises, with 1 mol. H_2O, in slender prisms having a silky lustre; dissolves in 100 parts of cold and 3 parts of boiling water, easily in alcohol; melts at about 200°, and splits up at 210°-220° into CO_2 and pyrogallol, $C_6H_3(OH)_3$. The aqueous solution reduces the metals from solutions of gold and silver salts (hence its use in photography), and forms a blue-black precipitate with ferric chloride.

Gallic acid, though monobasic, contains 3 atoms of phenolic hydrogen, and can therefore form tetrametallic salts. The gallates of the alkali-metals are permanent in the dry state and in acid solution, but in alkaline solution they quickly absorb oxygen and turn brown.

Ethyl gallate, $C_6H_2(OH)_3.CO_2C_2H_5$, crystallises from water in rhombic prisms containing $2\frac{1}{2}$ mol. H_2O. *Triacetyl-gallic acid*, $C_6H_2(OC_2H_3O)_3.CO_2H$, formed by heating gallic acid with acetyl chloride or acetic anhydride, crystallises from alcohol in needles. With bromine gallic acid forms $C_7H_5BrO_5$ and $C_7H_4Br_2O_5$, both of which are crystalline.

Gallic acid, heated with 4 parts of sulphuric acid to 140°, is converted into rufigallic acid, $C_{14}H_8O_8$, a derivative of anthracene (p. 590).

Ellagic acid, $C_{14}H_8O_9$, probably also an anthracene derivative, is formed by the action of oxidising agents—as arsenic acid, silver oxide, iodine and water—on gallic acid; also from tannic acid when its concentrated aqueous solution is left for a considerable time in contact with the air, the ellagic acid then separating, together with gallic acid. It is a constituent of bezoar stones (intestinal concretions of a Persian species of goat), from which it may be obtained by boiling with potash and precipitating with hydrochloric acid. It separates, with 1 mol. H_2O, as a crystalline powder, insoluble in water, and having an acid reaction. Its sodium salt is formed by boiling ethyl gallate with sodium carbonate.

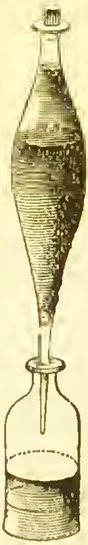
Tannic Acids or Tannins.

These substances constitute the astringent principles of plants, and are very widely diffused in the vegetable kingdom. Most of them are glucosides of gallic acid, being resolved by boiling with dilute acids into gallic acid and glucose; others, instead of glucose, yield phloroglucin, $C_6H_3(OH_3)_3$ (p. 498). Gallotannic acid, on the other hand, when quite pure, is not a glucoside, but consists of digallic acid. By fusion with potash most tannic acids are resolved into protocatechuic acid and phloroglucin.

Most tannic acids give bluish-black precipitates with ferric salts (inks); some, however, as kino and catechu, and the tannins of sumach and of the tea-plant, give greenish precipitates. The tannic acids precipitate a solution of gelatin, and unite with animal membranes: hence their use in the manufacture of leather. They are precipitated from their solutions by neutral acetate of lead.

Gallotannic Acid, Digallic Acid or **Tannin,** $C_{14}H_{10}O_9 = C_6H_2(OH)_3—CO—O—C_6H_2(OH)_3—CO_2H$, occurs in large quantity in nut-galls, especially in the Chinese variety, also in sumach (the twigs of *Rhus Coriaria*), in tea, and many other plants. It may be formed from gallic acid by heating with $POCl_3$ to 120°, and by oxidation with silver nitrate or dilute arsenic acid. It is most readily prepared by exhausting finely pulverised nut-galls with a mixture of alcohol and ether in a percolator (fig. 18), having its neck plugged with cotton-wool, and its mouth loosely stopped with a cork. The liquid, which after some time collects in the receiver below, consists of two distinct strata: the lower, which is almost colourless, is a very strong solution of almost pure tannic acid in water; the upper consists of ether, holding in solution gallic acid, colouring matter, and other impurities. The carefully separated heavy liquid is left to evaporate in an exsiccator. Gallotannic acid, or *tannin*, thus obtained, forms a slightly yellowish, friable, porous mass, without the slightest tendency to crystallisation. It is very soluble in water, less so in alcohol, and very slightly soluble in ether. It reddens litmus, and has a pure astringent taste without bitterness.

Fig. 18.



A strong solution of gallotannic acid mixed with mineral acids gives precipitates consisting of combinations of the tannic acid with the mineral acids; these compounds are freely soluble in pure water, but nearly insoluble in acid liquids. Gallotannic acid precipitates albumin, gelatin, salts of the vegeto-alkalis, and several other substances: it forms soluble compounds with the alkalis, which, if excess of base is present, rapidly attract oxygen, and become brown by destruction of the acid; the gallotannates of *barium, strontium,* and *calcium* are sparingly soluble ; those of *lead* and *antimony* are insoluble. Ferrous salts are unchanged by solution of gallotannic acid ; *ferric salts*, on the contrary, give with it a deep bluish-black precipitate, which is the basis of writing-ink : hence the value of an infusion of tincture of nut-galls as a test for the presence of iron.

Gallotannic acid decomposes at 250°, with formation of pyrogallol. By boiling with alkalis or dilute acids it is converted into gallic acid, $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$: hence its constitution is determined. By boiling with excess of acetic anhydride it is converted into pentacetyl-tannic acid, $C_{14}H_5(C_2H_3O)_5O_9$, a crystalline substance, melting at 137°.

The following tannins, which are amorphous bodies, more or less resembling gallotannic acid, have not been obtained in the pure state.

Quercitannic acid, from oak-bark, is a yellow-brown amorphous mass, the aqueous solution of which is coloured deep blue by ferric chloride. *Cinchona-tannic acid*, occurring in cinchona barks, partly in combination with alkaloïds, gives a green colour with ferric salts. *Ratanhia-tannic acid* occurs in rhatany-root ; *filitannic acid* in fern-roots ; *tormentil-tannic acid* in tormentil-root. These five tannins, when boiled with dilute acids, yield red amorphous bodies (oak-red, cinchona-red, &c.), which partly also occur ready-formed in the respective plants, and are resolved by fusion with potash into protocatechuic acid and phloroglucin. The formation of these red compounds appears to be accompanied by that of sugar.

Catechu-tannic acid occurs in catechu, an extract prepared from several East Indian plants, viz., *Areca Catechu*, *Acacia* (*Mimosa*) *Catechu*, and *Nauclea Gambir*. Ferric salts colour it dingy green. Catechu also contains catechin or catechuic acid, $C_{19}H_{18}O_8$, which crystallises in needles containing $3H_2O$. Its aqueous solution is coloured green by ferric salts. Anhydrous catechin melts at 217°, decomposing at the same time into CO_2 and pyrocatechin. By fusion with potash it is resolved into protocatechuic acid and phloroglucin :

$$C_{19}H_{18}O_8 + 2H_2O = C_7H_6O_4 + 2C_6H_6O_3 + 2H_2.$$

Morintannic acid or *Maclurin*, occurring in fustic (the wood of *Morus tinctoria*), is a yellow crystalline powder, easily soluble in hot water and in alcohol, the solutions giving with ferric chloride a greenish-black precipitate. It yields pyrocatechin when heated, phloroglucin and protocatechuic acid when fused with potash.

Caffetannic acid, from coffee-berries, is a gummy, easily soluble mass, which gives a green reaction with ferric chloride, yields pyrocatechin when heated alone, caffeic acid (p. 545), when heated with potash-solution ; protocatechuic acid when fused with potash.

Quinic or **Kinic Acid**, $C_7H_{12}O_6 = C_6H_7(OH)_4(CO_2H)$, is a monobasic pentatomic acid, nearly related to the aromatic oxy-acids. It is found in cinchona-bark, and is obtained as a bye-product in the preparation of quinine. The extract, obtained by digesting the comminuted bark with water or dilute sulphuric acid, is mixed with milk of lime to precipitate the alkaloïd; the solution is filtered and evaporated; and the calcium quinate which remains is purified by crystallisation, and decomposed with oxalic acid.

Quinic acid forms transparent colourless monoclinic prisms, easily soluble in water, very slightly soluble in alcohol. It melts at 162°, and at a higher temperature is resolved into hydroquinone, pyrocatechin, benzoic acid, phenol, and other products. By oxidising agents (MnO_2 and sulphuric acid) it is converted into quinone, together with carbonic and formic acids. By heating with hydriodic acid it is converted into benzoic acid:

$$C_6H_7(OH)_4.CO_2H + 2HI = C_6H_5.CO_2H + 4H_2O + I_2;$$

and by phosphorus pentachloride into chlorobenzoyl chloride:

$$C_6H_7(OH)_4.CO_2H + PCl_5 = C_6H_4Cl.COCl + PO_4H_3 + 3HCl + H_2O$$

By fusion with potash it yields protocatechuic acid.

Calcium quinate, $(C_7H_{11}O_6)_2Ca + 10H_2O$, forms large easily soluble efflorescent rhombic prisms.

Uvic Acid, $C_7H_8O_3$, obtained by distillation of pyrotartaric acid, forms shining crystals melting at 134° and sublimable; converted into benzoic acid by fusion with potash. Its calcium salt $(C_7H_7O_3)_2Ca + 6H_2O$ crystallises in needles.

Aldehydic acids.

These are acids containing the group CHO as well as CO.OH, in place of hydrogen, and exhibiting an aldehydic as well as an acid character. All the known aldehydic acids likewise contain the group OH, and are therefore the intermediate aldehydes of bibasic triatomic acids. They are produced, like salicylic aldehyde (p. 510) by the action of chloroform on the oxy-acids in alkaline solution.

Aldehydo-oxybenzoic Acid, $C_8H_6O_4 = C_6H_3(OH){<}\begin{matrix}CHO\\CO_2H\end{matrix}$. — Two isomeric acids of this composition (α and β *Aldehydosalicylic acids*), are obtained by boiling 14 parts of salicylic acid, 25 parts of sodium hydroxide, 50 parts of water, and 15 of chloroform, in a vessel with reversed condenser. On diluting with water, acidulating with hydrochloric acid, agitating with ether, and then agitating the concentrated ethereal solution with acid sodium sulphite, a solution is obtained, from which, after removal of the ether, sulphuric acid separates the β-acid as a crystalline powder, while the α-acid, together with a very small quantity of the β-acid, remains dissolved, and may be extracted from the solution by ether. A third acid, *γ-aldehydoparaoxybenzoic acid*, is obtained in like manner from paraoxybenzoic acid, together with paraoxybenzoic aldehyde.

α. ($CO_2H : OH : CHO = 1 : 2 : 3$).—Slender felted needles, sublimable when slowly heated. Much more soluble in water than β. Solution coloured red by ferric chloride. Calcium salt easily soluble : distilled with calcium hydrate gives salicylic aldehyde.

β. ($CO_2H : OH : CHO = 1 : 2 : 5$).—Slender needles melting at 249°, sublimable when slowly heated. Nearly insoluble in cold water, sparingly soluble in boiling water and cold alcohol, easily in hot alcohol and ether. Deep cherry-red with ferric chloride. Calcium salt very soluble ; distilled with CaH_2O_2 gives paraoxybenzaldehyde.

γ. ($CO_2H : OH : CHO = 1 : 3 : 4$).—Prismatic crystals, melting at 243°–244°, sublimable. Slightly soluble in cold, more readily in hot water, easily in alcohol and ether. Brick-red with ferric chloride. Calcium salt slightly soluble ; distilled with lime gives salicylic aldehyde.

Aldehydovanillic or **Aldehydo-methylprotocatechuic Acid,** $C_9H_8O_5 = C_6H_2(OH)(OCH_3){<}\begin{matrix}CHO\\CO_2H\end{matrix}$, is obtained, together with vanillin (p. 512) from vanillic acid, in the same manner as the aldehydoxybenzoic acids from the oxybenzoic acids. Crystallises in slender silky needles, melting at 221°–222°, slightly soluble in water, easily in alcohol and ether. Ferric chloride colours the solution violet.

Opianic Acid, $C_{10}H_{10}O_5 = C_6H_2(OCH_3)_2{<}\begin{matrix}CHO\\CO_2H\end{matrix}$.—*Aldehydo-dimethylprotocatechuic acid,* is formed, together with cotarnine and hemipinic acid (p. 553), in the oxidation of narcotine by MnO_2 and sulphuric acid, or with dilute nitric acid. It crystallises in slender, colourless prisms, melting at 140°, slightly soluble in cold water. Heated with soda-lime, it is converted into dimethyl-protocatechuic aldehyde, $C_6H_3(OCH_3)_2.CHO$ (p. 513), and when treated with oxidising agents, it yields hemipinic acid.

Meconin, $C_{10}H_{10}O_4$, occurs in opium, and is formed, together with cotarnine (see ALKALOIDS), from narcotine, by heating with water to 100°, and from opianic acid by the action of nascent hydrogen or of potash-ley. Shining colourless crystals, sparingly soluble in cold, more freely in hot water, melting at 110°. Heated with acids, it forms ethereal compounds, with elimination of water.

BIBASIC AND DIATOMIC ACIDS.

Benzene-dicarbonic Acids.

Acids, $C_8H_6O_4 = C_6H_4(CO_2H)_2$.

1. **Phthalic Acid** (1 : 2).—*Orthobenzene-dicarbonic acid* is formed by the action of nitric acid on naphthalene, dichloride of naphthalene, alizarin, and purpurin (the colouring matters of madder) :

$$\underset{\text{Naphthalene.}}{C_{10}H_8} + O_8 = \underset{\text{Phthalic acid.}}{C_8H_6O_4} + \underset{\text{Oxalic acid.}}{C_2H_2O_4}$$

$$\underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2H_2O + O_{10} = \underset{\text{Phthalic acid.}}{C_8H_6O_4} + \underset{\text{Oxalic acid.}}{3C_2H_2O_4}$$

$$\underset{\text{Purpurin.}}{C_{14}H_8O_5} + 2H_2O + O_9 = \underset{\text{Phthalic acid.}}{C_8H_6O_4} + \underset{\text{Oxalic acid.}}{3C_2H_2O_4}.$$

It is also produced by oxidising orthotoluic acid with permanganate solution, and is usually prepared by treating naphthalene dichloride at the boiling heat with nitric acid. Chromic acid mixture cannot be used in its preparation, as it is easily oxidised thereby to carbonic acid.

Phthalic acid crystallises in short prisms or laminæ, slightly soluble in cold water, easily soluble in hot water, alcohol, and ether. It melts at 185°, and is resolved at a higher temperature into water and phthalic anhydride, $C_8H_4O_3$. Heated with excess of calcium hydrate, it is resolved into $2CO_2$ and benzene, but when 2 molecules of it are heated with 1 mol. CaH_2O_2, it yields calcium benzoate:

$$2C_8H_6O_4 + CaH_2O_2 = (C_7H_5O_2)_2Ca + 2CO_2 + 2H_2O.$$

It forms both acid and neutral salts. Barium chloride added to the solution of its ammonium salt throws down barium phthalate, $C_8H_4O_4Ba$, which is very slightly soluble in water.

Phthalic acid is converted by fuming nitric acid into nitrophthalic acid, $C_8H_5(NO_2)O_4$.

Phthalic chloride, $C_8H_4(COCl)_2$, formed by heating the acid with PCl_5, is a liquid which boils at 270°, and is converted by zinc and hydrochloric acid into phthalic aldehyde, $C_6H_4(CHO)_2$, which crystallises from hot water in plates, and melts at 65°.

Phthalic anhydride, $C_6H_4{<}^{CO}_{CO}{>}O$, obtained by heating the acid, forms large needles, melts at 128°, and boils at 277°.

Hydrophthalic acid, $C_8H_8O_4$, formed by the action of sodium-amalgam on phthalic acid, dissolved in aqueous sodium carbonate, crystallises in tables; dissolves easily in hot water and alcohol; and melts at about 200°, decomposing at the same time into phthalic anhydride, water, and hydrogen. By the action of strong sulphuric acid, or by oxidation with nitric acid, chromic acid, or bromine and water, it is converted into benzoic acid. Tetrahydrophthalic acid, $C_8H_{10}O_4$, is prepared by heating its anhydride with water, and the anhydride, $C_8H_8O_3$, is produced by distillation of isohydropyromellitic acid (p. 555). The anhydride crystallises in laminæ melting at 68°. The acid also crystallises in laminæ, melting at 96°, and decomposing at the same time into water and the anhydride. Hexhydrophthalic acid, $C_8H_{12}O_4$, is obtained from either of the preceding by the action of sodium-amalgam, or by heating with hydriodic acid to 230°; it crystallises in prisms or laminæ, sparingly soluble in water, melting at 207°.

Isophthalic Acid, $C_6H_4(CO_2H)_2$ (1 : 3), is formed by oxidation of meta-xylene or metatoluic acid with chromic acid mixture, also by fusing metasulphobenzoate, or metabromobenzoate, or benzoate of potassium with potassium formate (in the last two cases together with terephthalic acid), and by the action of heat on hydropyromellitic and hydroprehnitic acid (p. 555). It crystallises in slender needles, soluble in 460 parts of boiling and 7800 parts of cold water, melts above 300°, and sublimes in needles without blackening. Its barium salt dissolves easily in water, so that the acid is not precipitated by barium chloride from the solution of its ammonium salt, a character by which it is distinguished from its two isomerides.

Methyl isophthalate, $C_6H_4(CO_2.CH_3)_4$, crystallises in needles, melting at 64°–65°. The *ethylic ether* is a colourless liquid, boiling at 285°, and not solidifying at 0°.

Nitrosophthalic acid, $C_6H_5(NO_2)O_4$, forms laminæ, melting at 249°.

Isophthalyl chloride, $C_6H_4(COCl)_2$, forms a radio-crystalline mass, melts at 41°, boils at 276°.

Terephthalic Acid, $C_6H_4(CO_2H)_2$ (1 : 4), is formed by oxidation of various bodies belonging to the para-series—as paraxylene, paratoluic acid, cumenol, and cymene, with chromic acid mixture. It is a white powder, crystalline if slowly deposited from solution, nearly insoluble in water, alcohol, and ether; sublimes undecomposed without previous fusion.

The *terephthalates,* $C_8H_4O_4Ca + 3H_2O$ and $C_8H_4O_4Ba + 4H_2O$, are crystalline, and very sparingly soluble. The methylic and ethylic ethers crystallise in prisms, the former melting at 104°, the latter at 44°.

Nitroterephthalic acid is crystalline, and melts at 259°. *Hydroterephthalic acid,* $C_8H_8O_4$, is a white powder, like terephthalic acid.

2. **Acids,** $C_9H_8O_4 = C_6H_3(CH_3)(CO_2H)_2$.

Uvitic Acid, ($CO_2H : CH_3 : CO_2H = 1 : 3 : 5$), is produced, together with mesitylenic acid, by prolonged boiling of mesitylene with dilute nitric acid, and by boiling pyruvic acid (p. 356) with barium hydrate. Slender needles, melting at 287°, sparingly soluble in hot water, easily in alcohol and ether; converted by oxidation with chromic acid into trimesic acid, and resolved by distillation with lime, first into CO_2 and metatoluic acid, afterwards into CO_2 and toluene.

Xylidic Acid, ($CO_2H : CH_3 : CO_2H = 1 : 3 : 4$), is produced from pseudocumene (p. 431), xylic acid, and paraxylic acid (p. 529), by prolonged boiling with dilute nitric acid. Indistinct colourless crystals, melting at 280°–283°, nearly insoluble in cold water.

Isoxylidic acid, formed by fusing potassium toluene-disulphonate with sodium formate, is very much like xylidic acid, but melts at 310°–315°.

Isouvitic acid, formed together with phloroglucin, pyrotartaric acid, and acetic acid, by fusing gamboge with potash, crystallises in short thick prisms, melting at about 160°.

3. **Acids,** $C_{10}H_{10}O_4$.

Cumidic acid, $C_6H_2(CH_3)_2(CO_2H)_2$, formed from durene and durylic acid by prolonged boiling with dilute nitric acid, crystallises in long transparent prisms, and sublimes at a high temperature.

Phenylene-diacetic acid, $C_6H_4(CH_2.CO_2H)_2$, is formed from $C_6H_4(CH_2Cl)_2$ (p.441). Long needles, melting at 244°, and subliming.

BIBASIC AND TRIATOMIC ACIDS.

Phenoldicarbonic Acid, $C_8H_6O_5 = C_6H_3(OH)(CO_2H)_2$, is formed, together with phenol and phenoltricarbonic acid, when basic sodium salicylate is heated to 360°–380° for several hours, with frequent agitation, in a stream of carbon dioxide. The product is dissolved in water, acidulated with hydrochloric acid, boiled, filtered hot, neutralised with ammonia and mixed with barium chloride, whereby barium phenoltricarbonate is precipitated. The liquid filtered after cooling and mixed with hydrochloric acid, deposits a mixture of phenoldicarbonic and salicylic acids, from which the latter may be dissolved out by chloroform. Phenoldicarbonic acid crystallises from boiling water in long needles, melts above 270°, and sublimes at 200°, with partial resolution into CO_2 and phenol. Slightly soluble in water, easily in alcohol and ether.

Oxyisouvitic Acid, $C_9H_8O_5 = C_6H_2(OH)(OCH_3)(CO_2H)_2$.—The ethylic ether of this acid is formed by the action of chloroform, chloral, carbon tetrachloride or ethyl trichloracetate on ethyl acetoacetate (p. 314). The free acid forms needles, sparingly soluble in cold water, more freely in hot water, easily in alcohol and ether. Ferric chloride colours its solution reddish violet. The barium salt, $C_9H_6O_5Ba + 1\frac{1}{2}H_2O$, heated with lime, yields metacresol. By oxidation with permanganate or dilute nitric acid, oxyisouvitic acid is converted into an acid isomeric with uvic acid (p. 549). It is insoluble in chloroform.

Hemipinic Acid, $C_{10}H_{10}O_6 = C_6H_2(OCH_3)_2.(CO_2H)_2$, formed, together with cotarnine, meconin, and opianic acid, by oxidation of narcotine, crystallises in large hydrated prisms slightly soluble in water. The dehydrated acid melts at 180°. By heating with HI, it is resolved into CO_2, methyl iodide, and protocatechuic acid: $C_{10}H_{10}O_6 + 2HI = C_7H_6O_4 + 2CH_3I + CO_2$.

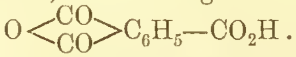
TRIBASIC ACIDS.

Benzenetricarboníc Acids, $C_9H_6O_6 = C_6H_3(CO_2H)_3$.

Trimesic acid (1:3:5).—Obtained by oxidation of mesitylenic or uvitic acid with chromic acid mixture; also by heating mellitic acid with glycerin in an oil-bath till the mass solidifies and begins to blacken; and, together with CO_2 and benzene-tetracarbonic acid, by heating hydro- and isohydromellitic acid with strong sulphuric acid. Short colourless prisms, rather sparingly soluble in cold water, easily in hot water, in alcohol, and in ether; melts above 300°, and sublimes without carbonisation. By heating with excess of lime it is resolved into CO_2 and benzene. The *ethylic ether*, $C_6H_3(CO_2C_2H_5)_3$, forms long silky prisms melting at 129°.

Hemimellitic acid (1:2:3), formed, together with phthalic anhydride, by heating hydromellophanic acid (p. 555) with strong sulphuric acid, crystallises in colourless needles somewhat sparingly soluble in water. It melts at about 185°, and is resolved at a higher temperature into phthalic anhydride and benzoic acid.

Trimellitic acid (1:2:4), is produced, together with isophthalic acid and pyromellitic anhydride, by heating hydropyromellitic acid with strong sulphuric acid, and abundantly, together with isophthalic acid in the oxidation of colophony by nitric acid. It forms nodular groups of indistinct crystals, moderately soluble in water and in ether; melts at 218°, giving off water at the same time, and being converted into the anhydride, $C_9H_4O_5$ =



$O\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_6H_5—CO_2H$.

Phenol-tricarbonic Acid, $C_9H_6O_7 = C_6H_2(OH)(CO_2H)_3$, is formed, together with phenol-dicarbonic acid, by heating sodium salicylate in a stream of carbon dioxide, and separated as a barium salt in the manner above described (p. 553). The free acid crystallises from a hot concentrated aqueous solution in thick prisms, containing $1H_2O$; from dilute solutions in needles with $2H_2O$. Heated above 180°, it is resolved, without previous fusion, into CO_2, phenoldicarbomic acid, salicylic acid, and phenol. The *ethylic ether*, $C_9H_3(C_2H_5)_3O_7$, forms long needles, melting at 84°.

QUADRIBASIC ACIDS.

Benzotetracarbonic Acids, $C_6H_2(CO_2H)_4$.

There are three possible modifications of these acids, all of which have been obtained.

(1.) Pyromellitic acid (1:2:4:5), is obtained as anhydride, $C_{10}H_2O_6$, by distillation of mellitic acid, or better, by heating sodium mellitate with sulphuric acid: $C_{12}H_6O_{12} = C_{10}H_2O_6 + 2CO_2 + 2H_2O$. The anhydride boiled with water yields the acid.

Pyromellitic acid crystallises with $2H_2O$ in prisms slightly soluble in cold water, easily in hot water and in alcohol. It melts at 264°, and is converted by distillation into the anhydride, $C_{10}H_2O_6$, which forms large crystals melting at 286°. The salts, $C_{10}H_2Ba_2O_8$ and $C_{10}H_2Ca_2O_8$, are white insoluble precipitates. The *ethylic ether*, $C_6H_2(CO_2.C_2H_5)_4$, forms short needles melting at 53°.

Hydropyromellitic and *Isohydropyromellitic acids*, $C_{10}H_{10}O_8 = C_6H_2(H_4)(CO_2H)_4$, are formed simultaneously by the action of sodium-amalgam on pyromellitic acid. The former remains on evaporating its ethereal solution as a very soluble mass. The latter crystallises with $2H_2O$, gives off its water at 120°, melts at about 200°, and is resolved into water, CO_2, and tetrahydrophthalic anhydride. Both acids, when heated with sulphuric acid, give off CO_2 and are converted into trimellitic and isophthalic acids.

(2.) Isopyromellitic or Prehnitic acid (1:2:3:5), is formed, together with CO_2, trimesic acid and mellophanic acid, by heating hydro- and isohydromellitic acid with strong sulphuric acid. It crystallises in groups of large prisms containing $2H_2O$; dissolves easily in water, and is separated from its concentrated solution by hydrochloric acid in crystals; melts at 238°, with formation of anhydride.

Hydroprehnitic acid, prepared like hydropyromellitic acid, is a gummy mass, resolved by heating with strong sulphuric acid into CO_2, prehnitic acid and isophthalic acid.

(3.) Mellophanic acid, produced, together with prehnitic acid, forms small indistinct anhydrous crystals united in crusts; melts at 215°–238°. With sodium-amalgam it yields hydromellophanic acid.

HEXATOMIC ACID.

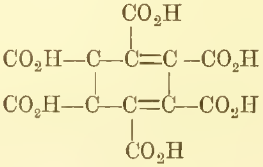
Mellitic Acid, $C_{12}H_6O_{12} = C_6(CO_2H)_6$.—This acid, having the constitution of benzene in which all the six hydrogen-atoms are replaced by carboxyl, occurs as aluminium salt in *mellite* or *honey-stone*, a mineral found in beds of lignite. It is soluble in water and alcohol, and crystallises in colourless needles, melts when heated, and is resolved by distillation into CO_2, water, and pyromellitic anhydride; by heating with lime, into CO_2 and benzene. It is a very stable acid, not being decomposed by sulphuric, nitric, or hydriodic acid, or by bromine; even with the aid of heat. Mellitic acid forms acid and neutral salts and ethers, whose composition may be illustrated by the following examples:

Neutral.	*Acid.*
$C_{12}(NH_4)_6O_{12}$	$C_{12}H_4(NH_4)_2O_{12}$
$C_{12}(CH_3)_6O_{12}$	$C_{12}H_3K_3O_{12}$
$C_{12}(C_2H_5)_6O_{12}$	$C_{12}H_3(C_2H_5)_3O_{12}$
$C_{12}Ba_3O_{12}$	$C_{12}H_2Cu_2O_{12}$
$C_{12}(Al_2)^{vi}O_{12}$	

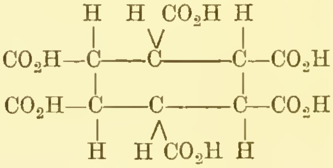
Ammonium mellitate yields by distillation paramide and euchroic acid. The former is a white amorphous substance, containing $C_{12}H_3N_3O_6$ (*i.e.*, tri-ammonic mellitate, $C_{12}H_3(NH_4)_3O_{12} - 6H_2O$), and convertible by boiling with water into acid ammonium mellitate. *Euchroic acid*, $C_{12}H_4N_2O_8[=C_{12}H_4(NH_4)_2O_{12}-4H_2O]$, forms colourless sparingly soluble crystals. In contact with zinc and deoxidising agents in general, it yields a deep blue insoluble substance called *euchrone*.

Hydromellitic acid, $C_{12}H_{12}O_{12}=C_6H_6(CO_2H)_6$, is slowly formed by the action of sodium-amalgam on ammonium mellitate. Colourless indistinct crystals, easily soluble in water. Sexbasic. Changes slowly by keeping, quickly, when heated to 180° with strong hydrochloric acid, into isohydromellitic acid, $C_{12}H_{12}O_{12}$, which crystallises in thick, hard four-sided prisms, dissolves readily in water, and is precipitated from the solution by hydrochloric acid. Both these acids, heated with strong sulphuric acid, yield a mixture of prehnitic, mellophanic, and trimesic acids.

Hydromellitic acid is an additive compound, in which the double linking of the alternate pairs of carbon-atoms in the benzene nucleus is broken up by the entrance of the additional hydrogen-atoms:



Mellitic.

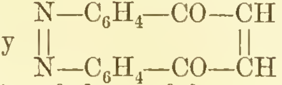


Hydromellitic.

INDIGO GROUP.

Indigo-blue and its immediate derivatives form a group of bodies nearly related to the benzene-group, as shown by their products of decomposition (aniline, ortho-amidobenzoic acid, &c.); but their constitution cannot yet be regarded as precisely determined, for want of sufficiently definite modes of synthetic formation.

Indigo-blue or **Indigotin**, C_8H_5NO or $C_{16}H_{10}N_2O_2$, probably



$$\begin{array}{l}N-C_6H_4-CO-CH\\ \| \qquad\qquad\qquad\quad \|\\ N-C_6H_4-CO-CH\end{array}$$

.—Indigo is the product of several species of plants of the genus *Indigofera*, growing in India and South America, also of *Isatis tinctoria*, *Nerium tinctorium*, *Polygonum tinctorium*, and other plants. It does not exist in these plants ready-formed, but is produced by decomposition of a glucoside, $C_{26}H_{31}NO_{17}$, called indican, which may be extracted from them by cold alcohol, and forms a brown bitter syrup, easily soluble in water and alcohol. This substance, when boiled with dilute acids, or subjected to the action of ferments, is resolved into indigo-blue and indiglucin, $C_6H_{10}O_6$:

$$C_{26}H_{31}NO_{17} + 2H_2O = C_8H_5NO + 3C_6H_{10}O_6.$$

A substance similar to indican sometimes occurs in urine, and gives rise, by its conversion into indigo-blue, to a blue coloration of the liquid when left in contact with the air, or treated with sulphuric acid.

To obtain indigo from the plants which produce it, the chopped leaves and twigs are macerated in water for 12 to 15 hours, after which the liquid is poured off into shallow wooden vessels, and frequently stirred, so as to bring it as much as possible into contact with the air. The indigo thereby deposited is separated from the brown liquid, boiled with water, and dried.

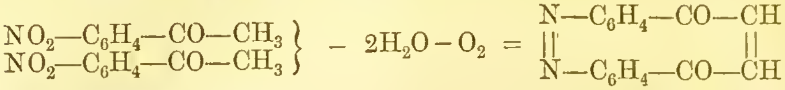
Commercial indigo is a mixture of several substances, all of which, except indigo-blue, are useless to the dyer. Boiling with dilute acetic acid extracts *indigo-gelatin;* dilute potash-ley then extracts *indigo-brown;* and the residue yields to boiling alcohol *indigo-red*, which remains on evaporation as a red powder, soluble in alcohol and ether. The residue left after boiling with alcohol is nearly pure indigo-blue.

Pure indigo-blue may be obtained from the commercial product by cautious sublimation; it then rises as a fine purple vapour, which condenses in dark-blue needles having a coppery lustre.

The best method of effecting the sublimation, is to mix 1 part of powdered indigo with 2 parts of plaster of Paris, make the whole into a paste with water, and spread it upon an iron plate. This, when quite dry, is heated by a spirit-lamp; the volatilisation of the indigo is aided by the vapour of water disengaged from the gypsum; and the surface of the mass becomes covered with beautiful crystals of pure indigo, which may be easily removed by a thin spatula. At a higher temperature, charring and decomposition take place.

The best method of obtaining indigo-blue is to reduce the crude product to indigo-white by the action of ferrous sulphate or glucose in alkaline solution, and then reoxidise it. It is on this principle that the dyer prepares his *indigo-vat:* 5 parts of powdered indigo, 10 parts of green vitriol, 15 parts of slaked lime, and 60 parts of water, are agitated together in a close vessel, and then left to stand. The ferrous hydrate, in conjunction with the excess of lime, reduces the indigo to the soluble state; and a yellowish liquid is produced, from which acids precipitate indigo-white, as a flocculent substance which absorbs oxygen with the greatest avidity, and becomes blue. Cloth, steeped in the alkaline liquid, and then exposed to the air, acquires a deep and permanent blue tint by the deposition of solid insoluble indigo in the substance of the fibre.—Instead of the iron salt and lime, a mixture of dilute caustic soda and grape-sugar dissolved in alcohol may be used; the sugar becomes oxidised to formic acid, and the indigo reduced. On allowing such a solution to remain in contact with the air, it absorbs oxygen, and deposits indigo-blue in the crystalline state.

Indigo-blue is said to have been obtained by treating liquid nitro-acetophenone (p. 514) dissolved in chlorform with a mixture of soda-lime, and zinc-dust, according to the equation,



$$\left.\begin{array}{l}NO_2-C_6H_4-CO-CH_3\\ NO_2-C_6H_4-CO-CH_3\end{array}\right\} - 2H_2O - O_2 = \begin{array}{l}N-C_6H_4-CO-CH\\ \| \qquad\qquad\qquad\qquad\quad \|\\ N-C_6H_4-CO-CH\end{array}$$

Nitro-acetophenone (2 mols.). Indigo-blue.

But the quantity of indigo-blue thus obtained is always very small, and it appears to be very difficult to ascertain the precise conditions under which the transformation takes place.*

Indigo-white or **Hydrindigotin**, $C_{16}H_{12}N_2O_2$, is precipitated by hydrochloric acid from its alkaline solution (formed as above), out of contact with the air, as a white crystalline powder, dissolving with yellow colour in alcohol, ether, and alkalis. It is converted into indigo-blue by exposure to the air, and into indol by distillation with zinc-dust.

Indigo-sulphonic Acids.—When indigo blue is heated for a considerable time with 8 to 15 parts of strong sulphuric acid, it dissolves, with formation of a mono- and di-sulphonic acid.

Indigo-monosulphonic acid, $C_{16}H_9N_2O_2.SO_3H$ (*Sulphopurphuric* or *Phœnicinsulphonic acid*), separates, on diluting the solution with water, as a blue powder, soluble in pure water and in alcohol, but insoluble in dilute acids. Its salts are red in the solid state, but dissolve in water with blue colour.

Indigo-disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$ (*Sulphindigotic* or *Sulphindylic acid*), remains in the filtrate from the monosulphonic acid, and constitutes the sole product when 15 parts of sulphuric acid are used to dissolve 1 part of indigo. To separate the acid, clean white wool, previously boiled with solution of sodium carbonate, is dipped into the liquid, and as soon as it has acquired a dark blue colour, it is taken out, washed with water, and boiled with ammonium carbonate; the resulting solution is precipitated with lead acetate, and the precipitate decomposed by hydrogen sulphide. In this manner a colourless solution of hydrindigotindisulphonic acid, $C_{15}H_{12}N_2O_2(SO_3H)_2$, is obtained, which, on exposure to the air, is quickly converted by oxidation into the disulphonic acid of indigo-blue, which, on evaporating the solution, remains in the form of a blue amorphous mass. The salts, $C_{16}H_8N_2O_2(SO_3K)_2$ and $C_{12}H_8N_2O_2(SO_3Na)_2$, known in commerce as indigo-carmine, are prepared on the large scale by adding potassium acetate or sodium sulphate to a dilute solution of indigo-blue in sulphuric acid, washing the blue precipitate with solutions of the same salts, and pressing it. They form copper-coloured masses, blue in the finely divided state, and dissolving with blue colour in pure water.

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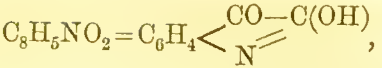
* Emmerling and Engler, Deutsch. Chem. Ges. Ber. ix. 1422; Chem. Soc. Journal, 1877, i. 321.

Isatin,  $C_8H_5NO_2=C_6H_4\Big\langle\begin{array}{l}CO-C(OH)\\ N=\!\!=\end{array}$, is obtained by oxidising indigo with chromic, or better, with nitric acid. Powdered indigo is mixed with water to a thin paste, heated to the boiling point in a large capsule, and nitric acid is added by small portions until the blue colour disappears; the whole is then largely diluted with boiling water, and filtered. The impure isatin which separates on cooling is washed with water containing a little ammonia, and recrystallised. The process requires careful management, or the oxidising action proceeds too far, and the product is destroyed.

Isatin forms deep yellowish-red prismatic crystals, sparingly soluble in cold water, freely in boiling water and in alcohol. The solution colours the skin yellow, and causes it to emit a very disagreeable odour. Isatin when heated melts and sublimes, with partial decomposition. It unites with acid sulphites of alkali-metal, forming crystalline compounds. It dissolves in alkalis, forming violet solutions, from which silver nitrate throws down a red precipitate of $C_8H_4AgNO_2$. On boiling these solutions, the isatin is converted into isatic acid, and the colour changes to yellow.

Isatin is converted by nitrous acid into nitrosalicylic acid. Distilled with strong potash-solution it yields aniline. On heating it to 80°, with phosphorus trichloride and phosphorus, dissolving the product in water, and leaving the solution exposed to the air for twenty-four hours, it deposits indigo-blue.

Chlorinated and *Brominated derivatives of Isatin* (mono- and di), *e.g.*, $C_8H_4ClNO_2$, $C_8H_3Cl_2NO_2$, &c., are formed by passing chlorine or bromine into the hot aqueous solution of isatin. These compounds crystallise well, and are converted by fusion with potash into substituted anilines; *e.g.*,

$$C_8H_4ClNO_2 + 4KOH = C_6H_4Cl.NH_2 + 2CO_3K_2 + H_2.$$

Isatin boiled with ammonia yields amido-derivatives, which have been but little examined. By reducing agents it is converted into isatyde, $C_{16}H_{12}N_2O_4$.

Isatinsulphonic acid, $C_8H_4NO_2.SO_3H$, formed by oxidation of indigosulphonates (indigo-carmine,) is very soluble, and crystallises with difficulty: it forms derivatives analogous to those of isatin.

Isatyde or Hydroisatin, $C_8H_6NO_2$, is formed when isatin is warmed with dilute sulphuric acid, or when its warm, saturated, alcoholic solution is mixed in a closed flask with ammonium hydrosulphide, the liquid then gradually depositing the isatyde in colourless crystalline scales. It is tasteless, insoluble in water, slightly soluble in alcohol.

Thioisatyde, $C_{16}H_{12}N_2S_2O_2$, is formed on passing hydrogen sulphide into an alcoholic solution of isatin, and is precipitated on dropping the filtered solution into water. It is a greyish-yellow, pulverulent, uncrystallisable substance, which softens in hot water, and dissolves in alcohol.

Indin, $C_{16}H_{10}N_2O_2$ (isomeric or polymeric with indigo-blue), is formed on triturating thioisatyde with potassium hydroxide, gradually adding alcohol, and washing the reddened mass with water; also by boiling a solution of dioxindol in glycerin. It is a crystalline powder of a fine rose-colour, insoluble in water, slightly soluble in alcohol. It dissolves when heated with alcoholic potash, and the solution, on cooling, deposits potassium-indin, $C_{16}H_9KN_2O_2$, in small black crystals.

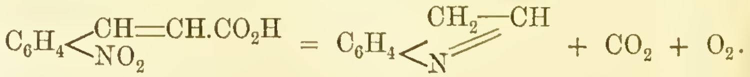
Isatic Acid or **Trioxindol**, $C_8H_7NO_3$.—The violet solution of isatin in potash-ley turns yellow when heated, and then contains *potassium isatate*, $C_8H_6KNO_3$, which is deposited on evaporation in yellow crystals. This salt, decomposed with an acid, yields isatic acid as a white powder, soluble in water, and resolved by heat into isatin and water.

Hydrindic Acid or **Dioxindol**, $C_8H_7NO_2$, is formed by the action of sodium on isatin suspended in water or dissolved in an alkali, isatic acid being first formed, and then reduced. It crystallises in yellow prisms, is soluble in water and in alcohol, and forms crystalline compounds both with bases and with acids. It melts at 180°, and decomposes at 195°, with formation of aniline. The aqueous solution turns red on exposure to the air, from formation of isatin: when boiled with ammonia it turns violet. Metallic salts added to the solution throws down crystalline compounds, such as $C_8H_6AgNO_3$ and $C_8H_5PbNO_3+H_2O$.

Dioxindol treated with nitrous acid in alcoholic solution, is converted into *nitroso-dioxindol*, $C_8H_6(NO)NO_3$, which, when heated with nitric acid or silver oxide, yields benzaldehyde.

Oxindol, C_8H_7NO, is formed by reduction of dioxindol with sodium-amalgam in acid solution, or with tin and hydrochloric acid, and crystallises in colourless needles, easily soluble in hot water, alcohol, and ether. It melts at 120°, and when heated in small quantities, may be sublimed without decomposition. It forms crystallisable salts, both with acids and with bases. Its aqueous solution, evaporated in an open vessel, is partially oxidised to dioxindol. Nitrous acid converts it into nitrosoxindol, $C_8H_9(NO)NO$, which crystallises in long golden-yellow needles, slightly soluble in water.

Indol, C_8H_7N, is formed by distilling oxindol over heated zinc-dust, and by fusing orthonitrocinnamic acid with potassium hydroxide and iron filings (to abstract oxygen):

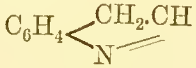


$$C_6H_4{<}\begin{matrix}CH{=}CH.CO_2H\\NO_2\end{matrix} = C_6H_4{<}\begin{matrix}CH_2{-}CH\\N{=\!\!=}\end{matrix} + CO_2 + O_2.$$

It is produced in larger quantity (about 0·5 per cent.) by digesting serum-albumin or egg-albumin with pancreatic juice.

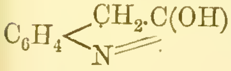
Indol crystallises from hot water in large, shining, colourless laminæ, resembling benzoic acid, and smelling like naphthylamine. It melts at 52°, boils with partial decomposition at about 245°, volatilises in a vacuum without decomposition, and distils easily with vapour of water. It is a weak base, its salts being decomposed by boiling with water. Its vapour colours a deal shaving moistened with hydrochloric acid, deep cherry-red. Its solution acidulated with hydrochloric acid is coloured rose-red by potassium nitrite. The reddish coloration is likewise produced by several other reagents. Indol fused with potash is converted into aniline (probably through the medium of ortho-amidobenzoic acid). Ozone passed through an aqueous solution of indol forms a small quantity of indigo-blue.

The formation of aniline from indol and its three hydroxyl-derivatives, by fusion with potash, and their conversion into anthranilic and nitrosalicylic acids by regulated oxidation with nitric acid, show that in these bodies the benzene-nucleus C_6H_4 is directly linked to carbon and to nitrogen, and that the OH groups are situated in the lateral chains. They may accordingly be represented by the following formula:



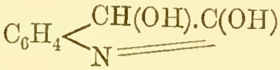
$$C_6H_4\left\langle\begin{array}{l}CH_2.CH\\ N\end{array}\right.$$

Indol.



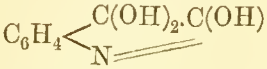
$$C_6H_4\left\langle\begin{array}{l}CH_2.C(OH)\\ N\end{array}\right.$$

Oxindol.



$$C_6H_4\left\langle\begin{array}{l}CH(OH).C(OH)\\ N\end{array}\right.$$

Dioxindol.



$$C_6H_4\left\langle\begin{array}{l}C(OH)_2.C(OH)\\ N\end{array}\right.$$

Trioxindol.

The formation of anthranilic (1 : 2 amidobenzoic) acid shows further that the lateral chains in these compounds occupy contiguous places.

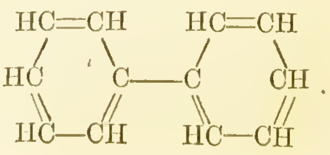
Indol is therefore an ortho-compound. An isomeric compound, which has a higher melting point (89°–91°), and does not yield indigo-blue when treated with ozone, is formed by heating albumin with excess of potassium hydroxide.

DIPHENYL GROUP.

The compounds of this group contain two or more benzene-nuclei, united either directly or through the medium of other carbon groups.

Hydrocarbons, C_nH_{2n-14}:

Diphenyl, $C_{12}H_{10} = C_6H_5.C_6H_5$ or



—This hydrocarbon is formed: (1.) By passing benzene-vapour through a red-hot tube containing fragments of pumice : $2C_6H_6 = C_{12}H_{10} + H_2$. This is the best method of preparing it, the yield amounting to about 30 per cent. of the benzene used.

(2.) By the action of sodium on bromobenzene (phenyl bromide) dissolved in ether or benzene :

$$2C_6H_5Br + Na_2 = 2NaBr + C_{12}H_{10}\,.$$

(3.) By heating a mixture of potassium phenate and benzoate or oxalate, and in small quantity (together with benzene) by heating benzoic acid with lime.

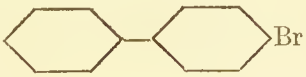
(4.) Together with other products, by the action of alcoholic potash on nitrate of diazobenzene :

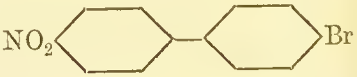
$$\underset{\text{Diazobenzene.}}{2C_6H_4N_2} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Diphenyl.}}{C_{12}H_{10}} + \underset{\text{Aldehyde.}}{C_2H_4O} + 2N_2\,.$$

Diphenyl appears also to be one of the constituents of crude anthracene (p. 582), and passes over in the distillation of that substance, at about 260°.

Diphenyl crystallises from alcohol in iridescent nacreous scales, melts at about 70·5°, sublimes at a higher temperature, and boils at 254°. When dissolved in glacial acetic acid it is oxidised by chromic anhydride to benzoic acid.

Diphenyl, subjected to the action of halogens, nitric acid, and sulphuric acid, yields mono- and di- substitution-derivatives. In the former, such as $C_{12}H_9Br$, $C_{12}H_9(NO_2)$, $C_{12}H_9(SO_3H)$, the substituted radicles stand to the place of junction of the two benzene-nuclei in the para-position. The di-derivatives are known in two isomeric modifications, the most frequent being those in which both the substituted groups are in the para-position relatively to the point of junction:


Monobromodiphenyl (para).


Nitro-bromodiphenyl (para-para).

By oxidation with chromic anhydride, the monosubstituted diphenyls yield para-derivatives of benzoic acid, the group C_6H_4Br, for example, being oxidised to (1:4) bromobenzoic acid, while the other group (C_0H_5) is broken up. The di-derivatives, on the other hand, are converted by oxidation into two para-derivatives of benzoic acid, *e.g.*, $C_6H_4(NO_2).C_6H_4Br$ into *p*-nitro and *p*-bromobenzoic acid.

Monochlorodiphenyl, $C_{12}H_9Cl$, formed by the action of PCl_5 on oxydiphenyl ($C_{12}H_0.OH$), forms colourless crystals melting at 75°. *Dichlorodiphenyl*, $C_{12}H_8Cl_2$, from benzidine, melts at 148°.

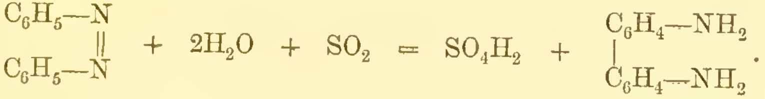
Bromodiphenyl, $C_{12}H_9Br$, forms laminæ, melts at 89°, boils at 310°. $C_{12}H_8Br_2$ forms prisms melting at 164°.

Cyanodiphenyl, $C_{12}H_0.CN$, obtained by dry distillation of a mixture of diphenyl-monosulphonate and cyanide of potassium, forms hard, colourless crystals, melting at 84°–85°, insoluble in water, easily soluble in alcohol. *Dicyanodiphenyl*, $C_{12}H_8(CN)_2$, obtained in like manner from diphenyldisulphonic acid, forms ramified colourless needles, melting at 234°, sparingly soluble in cold, freely in boiling alcohol.

Nitrodiphenyl, $C_{12}H_9(NO_2)$, crystallises in needles, melts at 113°, boils at 340°. An isomeric compound obtained by distilling calcium meta-nitrobenzoate with potassium phenate, melts at 86°, according to Pfankuch, at 157°, according to Schultz.* Two *dinitro-compounds*, $C_{12}H_8(NO_2)_2$, are formed by the action of fuming nitric acid on diphenyl; the less soluble in alcohol of the two melts at 213°, and boils at 340°; the more soluble compound melts at 93·5°.

Amidodiphenyls are formed by the reduction of the nitro-compounds with tin and hydrochloric acid.—*Xenylamine*, $C_{12}H_9(NH_2)$, crystallises from hot water or alcohol in colourless laminæ melting at 49°.

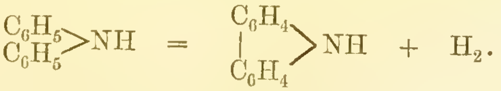
Benzidine, $C_{12}H_8(NH_2)_2$, is also produced by the action of sodium on monobromaniline, and by molecular transposition of hydrazobenzene in contact with acids (p. 467); further, by heating azobenzene with fuming hydrochloric acid to 115°, and by passing SO_2 into the alcoholic solution of that compound:



$$\begin{array}{l}C_6H_5\text{—}N\\ \qquad\ \|\\ C_6H_5\text{—}N\end{array} + 2H_2O + SO_2 = SO_4H_2 + \begin{array}{l}C_6H_4\text{—}NH_2\\ |\\ C_6H_4\text{—}NH_2\end{array}.$$

Benzidine crystallises in silvery laminæ, easily soluble in hot water and alcohol, melting at 118°, and subliming with partial decomposition. It is a biacid base. The *sulphate*, $C_{12}H_{12}N_2.SO_4H_2$, is nearly insoluble in water and alcohol.

Diphenylimide or Carbazol, $C_{12}H_9N$, is formed by passing the vapour of aniline or of diphenylamine through a red-hot tube:



$$\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>\!NH = \left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right>NH + H_2.$$

It occurs in coal-tar oil (320°–360°), and as a bye-product in the manufacture of aniline.

Carbazol crystallises in shining laminæ, soluble in hot alcohol, ether, and benzene; melts at 238°, and distils at 354°–355°. It dissolves in strong sulphuric acid, with yellow colour, easily changed to green by oxidising agents. With picric acid, it forms a compound which crystallises in red needles melting at 182°.

Acridine, $C_{12}H_9N$, isomeric with carbazol, likewise occurs in coal-tar oil, and may be extracted by sulphuric acid from the portion boiling between 320° and 360°. It forms rhombic crystals, easily soluble in alcohol and ether, melts at 107°, sublimes in broad needles at 100°, boils at a temperature above 360°. It unites with acids (carbazol does not) forming salts which are decomposed by boiling with a large quantity of water.

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* Liebig's Annalen, clxxiv. 201; Jahresbericht für Chemie, 1874, 405.

Diphenylsulphonic acids, $C_{12}H_9(SO_3H)$ and $C_{12}H_8(SO_3H)_2$, are formed by heating diphenyl with strong sulphuric acid, the former, however, only when a very small quantity of sulphuric acid is used. The disulpho-acid crystallises in long deliquescent prisms, melting at 72·5°. These acids fused with potash yield the corresponding phenols, $C_{12}H_9(OH)$ and $C_{12}H_8(OH)_2$.

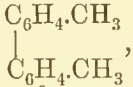
Hydrocarbons, $C_{13}H_{12}$:—

Phenyl-tolyl, $C_6H_5.C_6H_4.CH_3$, is formed by the action of sodium on a mixture of bromobenzene and parabromotoluene diluted with ether. It is a colourless liquid of specific gravity 1·015 at 27°, boiling at 263°–267°, solidifying in a freezing mixture.

Diphenylmethane, $C_{13}H_{12} = C_6H_5.CH_2.C_6H_5$ (*Benzyl-benzene*), is obtained by heating a mixture of benzene (6 parts) and benzyl chloride (10 parts) with zinc-dust (3 or 4 parts) in a vessel with reversed condenser. Colourless crystalline mass made up of needles, and having an odour of oranges; melts at 26°–27°, boils at 261°–262°; dissolves easily in alcohol and ether. Passed through a red-hot tube it yields diphenylene-methane, $C_{13}H_{10}$. Chromic acid mixture oxidises it to diphenyl ketone, $CO(C_6H_5)_2$. It dissolves in strong nitric acid, forming two dinitro-derivatives.

Diphenyl-chloromethane, $C_6H_5—CHCl—C_6H_5$, formed by the action of HCl on benzhydrol (p. 569), is a crystalline mass melting at 14°.

Hydrocarbons, $C_{14}H_{14}$:—

Ditolyl,  $\begin{array}{l} C_6H_4.CH_3 \\ | \\ C_6H_4.CH_3 \end{array}$, produced by the action of sodium on parabromotoluene, forms monoclinic crystals, easily soluble in hot alcohol, melting at 121°.

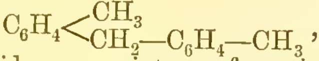
Dibenzyl, $= C_6H_5.CH_2.CH_2.C_6H_5$, formed by the action of sodium on benzyl chloride, and by heating stilbene, tolane, benzoïn, deoxybenzoïn, or toluylene hydrate, with hydriodic acid, crystallises in large colourless prisms, melts at 52°, boils at 284°; dissolves easily in hot alcohol. Heated to 500° it yields stilbene and toluene: $2C_{14}H_{14} = C_{14}H_{12} + 2C_7H_8$.

Diphenyl-ethane, $C_{14}H_{14} = (C_6H_5)_2CH - CH_3$, is formed by the action of sulphuric acid on a mixture of paraldehyde and benzene ($2C_6H_6 + C_2H_4O - H_2O = C_{14}H_{14}$). Colourless liquid, boiling at 268°–270°, solidifying in a freezing mixture: oxidised by chromic acid mixture to benzophenone.

A mixture of 2 mol. benzene and 1 mol. chloral or bromal with strong sulphuric acid, yields in like manner, diphenyltrichlorethane, $(C_6H_5)_2CH—CCl_3$ (colourless laminæ melting at 64°), or diphenyltribromethane $(C_6H_5)_2CH—CBr_3$ (monoclinic crystals, m. p. 89°). A mixture of benzene and dichlorethylic oxide, $(C_2H_4Cl)_2O$, similarly treated, yields *diphenyl-monochlorethane* $(C_6H_5)_2CH—CH_2Cl$, as an oil which decomposes when distilled.

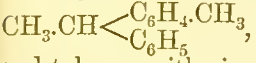
Benzyl-toluene, $C_{14}H_{14} = C_6H_5.CH_2.C_6H_4.CH_3$, formed by passing the vapours of paraphenyl-tolyl ketone, $C_6H_5.CO.C_6H_4(CH_3)$, over heated zinc-dust, is a colourless liquid boiling at 285°–286°, not solidifying at $-20°$.

Hydrocarbons, $C_{15}H_{16}$:—

Ditolyl-methane,  $C_6H_4{<}\begin{matrix}CH_3\\CH_2—C_6H_4—CH_3\end{matrix}$, formed by the action of sulphuric acid on a mixture of methylal, $CH_2(OCH_3)_2$ (p. 168), toluene, and glacial acetic acid, is a liquid not solidifying at $-15°$, boiling at 290°.—$C_{15}H_{14}Br_2$, forms long needles melting at 115°.—$C_{15}H_{14}(NO_2)_2$, forms colourless crystals melting at 164°.

Dibenzyl-methane, $C_6H_5.CH_2.CH_2.C_6H_5$, from dibenzyl ketone by heating with HI and phosphorus, is a non-solidifiable liquid, boiling at 290°–300°.

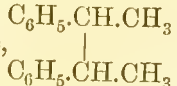
Benzyl-ethyl-benzene, $C_6H_5.CH_2.C_6H_4.C_2H_5$, from benzyl chloride and benzene, is a colourless liquid boiling at 294°–295°.

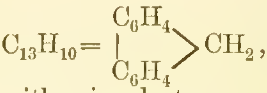
Ethyl-benzene-toluene or **Phenyltolyl-ethane,**  $CH_3.CH{<}\begin{matrix}C_6H_4.CH_3\\C_6H_5\end{matrix}$, formed by heating bromethyl-benzene (p. 441) and toluene with zinc-dust, is a liquid boiling at 278°–280°.

Hydrocarbons, $C_{16}H_{18}$:—

Ditolylethane, $CH_3—CH(C_6H_4.CH_3)_2$, obtained, like diphenylethane, from paraldehyde, toluene, and sulphuric acid, is a liquid, boiling at 295°–298°, not solidifying at $-20°$.

Similarly, by the use of chloral instead of paraldehyde, is obtained $CCl_3—CH(C_6H_4.CH_3)_2$, in crystals melting at 89°; and with dichlorethylic oxide, $CH_2Cl—CH(C_6H_4.CH_3)$.

Diphenyldimethylethane,  $\begin{matrix}C_6H_5.CH.CH_3\\|\\C_6H_5.CH.CH_3\end{matrix}$, obtained by the action of sodium on secondary phenyl-ethyl chloride, $C_6H_5.CHCl.CH_3$ (p. 503) forms needles melting at 123·5°.

Diphenylene-methane or Fluorene,  $C_{13}H_{10} = \begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}CH_2$, is formed by heating diphenylene ketone with zinc-dust or with hydriodic acid and amorphous phosphorus to 160°, also by passing the vapour of diphenyl-methane through a red-hot tube. It is contained in the portion of coal-tar oil boiling at 300°–305°. It crystallises from hot alcohol in colourless laminæ, exhibiting a beautiful violet fluorescence; melts at 112°–113°, boils at 305° ; unites with picric acid, forming a compound which crystallises in red needles melting at 80°–82°. By oxidation with chromic acid mixture it yields diphenylene-ketone, $CO(C_6H_4—C_6H_4)$.

Diphenyl-benzene, $C_{18}H_{14} = C_6H_4(C_6H_5)_2$, is formed by the action of sodium on a mixture of bromobenzene and paradibromobenzene, and, together with an isomeric compound, by passing a mixture of diphenyl and benzene through red-hot tubes: hence these two isomeric compounds are obtained, as secondary products, in the preparation of diphenyl.—Diphenylbenzene forms groups of needles slightly soluble in hot alcohol and ether, melting at 205°, subliming easily and boiling at 400°. By chromic anhydride and glacial acetic acid it is oxidised to diphenylcarbonic, and afterwards to terephthalic acid.—*Isodiphenyl-benzene* melts at 85°, and boils at about 360°.

Triphenyl-methane, $C_{19}H_{16} = C_6H_5—CH(C_6H_5)_2$, is formed by heating benzal chloride to 150° with mercury-diphenyl:

$$C_6H_5.CHCl_2 + (C_6H_5)_2Hg = HgCl_2 + C_6H_5—CH(C_6H_5)_2;$$

also by heating benzhydrol (p.569) with benzene and phosphoric anhydride to 140°:

$$(C_6H_5)_2CH.OH + C_6H_6 = (C_6H_5)_2CH(C_6H_5)_2 + H_2O.$$

Shining laminæ, melting at 92°, boiling at about 360°. By bromine and water it is converted into triphenyl carbinol, which melts at 157°.

Tolyl-diphenyl-methane, $C_{20}H_{18} = (C_6H_5)_2CH—C_6H_4—CH_3$, prepared, like the preceding, from benzhydrol and toluene, is a colourless liquid of high boiling point.

Triphenyl-benzene, $C_{24}H_{18} = C_6H_3(C_6H_5)_3$, obtained by heating acetophenone (p. 514) with phosphoric anhydride, forms large rhombic crystals, melts at 169°, boils above 360°, dissolves easily in alcohol and in benzene.

Tetraphenyl-ethane, $C_{26}H_{22} = (C_6H_5)_2CH—CH(C_6H_5)_2$, obtained by the action of zinc on a solution of benzhydrol, $C_6H_5.CHOH.C_6H_5$, mixed with fuming hydrochloric acid, forms large prisms melting at 209°.

Ethene-derivatives.

Diphenyl-ethene, $C_{14}H_{12}$.—Of this hydrocarbon there are two modifications, symmetrical and unsymmetrical.

1. *Stilbene* or *Toluylene,* $C_6H_5—CH{=}CH—C_6H_5$, is formed in a variety of reactions, especially by dry distillation of benzyl sulphide or disulphide (p. 562); by the action of sodium on benzaldehyde or benzal chloride; and by passing the vapour of dibenzyl or of toluene over heated lead oxide. It is most easily obtained from benzyl sulphide.

Stilbene crystallises in large laminæ, dissolves easily in hot alcohol, melts at 125°, distils at 306°–307°. By heating with hydriodic acid it is converted into dibenzyl; by oxidation with chromic acid mixture into benzaldehyde and benzoic acid. It unites with bromine, forming $C_{14}H_{12}Br_2$ (crystals, melting at 230°), which is also produced by the action of bromine, without cooling, on dibenzyl. By alcoholic potash this bromide is converted into bromostilbene, $C_{15}H_{11}Br$ (crystals, m. p. 25°), and tolane.

2. *Isostilbene*, $CH_2{=\!=}C(C_6H_5)_2$, *unsymmetric diphenylethene*, obtained by boiling diphenyl-monochlorethane (p. 565) with alcoholic potash, is a colourless non-solidifying oil, which boils at 277°, and is converted by oxidation into diphenyl-ketone.

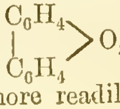
Tetraphenyl-ethene, $C_{26}H_{20} = (C_6H_5)_2C{=\!=}C(C_6H_5)_2$, obtained by the action of finely divided silver on benzophenone chloride, and, together with diphenyl-methane, and other hydrocarbons by heating, benzophenone with zinc-dust, is a white crystalline powder, melting at 221°, sparingly soluble in alcohol and ether, easily in benzene.

Tolane, $C_{14}H_{10} = C_6H_5—C{\equiv}C—C_6H_5$, *Diphenyl-acetylene*, obtained by boiling stilbene bromide with alcoholic potash, forms large crystals, melting at 60°, easily soluble in alcohol and ether. It forms two dibromides, $C_{14}H_{10}Br_2$ (m. p. 64° and 200°–205°), easily convertible one into the other; and two dichlorides (m. p. 63° and 153°).

Phenols.

Oxydiphenyl or **Diphenylol**, $C_{12}H_9.OH = C_6H_5—C_6H_4.OH$, is formed by fusing the potassium salt of diphenylsulphonic acid, $C_{12}H_9.SO_3H$, with potassium hydroxide, and by the action of potassium nitrite on amidodiphenyl sulphate. Colourless monoclinic crystals; melts at 164°–165°, boils at 305°–308°; volatilises with vapour of water; dissolves easily in alcohol, ether, and alkalis; and with fine green colour in strong sulphuric acid.

Dioxydiphenyl or **Diphenol**, $C_{12}H_8(OH)_2 = C_6H_4(OH).C_6H_4(OH)$ is formed by the action of melting potash on potassium diphenylparasulphonate; also from benzidine by the diazo-reaction; and by fusing potassium paraphenol-sulphonate with alkalis. Colourless rhombic crystals, melting at 156°–158°. An isomeric compound, which crystallises from alcohol in shining needles melting at 269°–270°, is formed by the action of melting potash on potassium diphenyl-disulphonate.

Diphenylene Oxide, $C_{12}H_8O =$  $\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right>O$, formed by heating phenyl phosphate with lime, or more readily by heating phenol with lead oxide, crystallises in laminæ, melts at 81°, and boils at 273°.

Hexoxydiphenyl, $C_{12}H_{10}O_6 = C_{12}H_4(OH)_6$, is formed from its tetramethylic ether (hydrocœrulignone) by the action of strong hydrochloric or hydriodic acid:

$$C_{12}H_4(OH)_2(OCH_3)_4 + 4HCl = 4CH_3Cl + C_{12}H_4(OH)_6.$$

It crystallises from water in silvery laminæ; dissolves in potash-ley with fine blue-violet colour; is converted by acetyl chloride into a hexacetyl compound; and reduced by heating with zinc-dust to diphenyl.

Hydrocœrulignone, $C_{12}H_4\left\{\begin{matrix}(OCH_3)_4\\(OH)_2\end{matrix}\right.$, is formed from cœrulignone by the action of tin and hydrochloric acid. It crystallises from alcohol in colourless laminæ, melts at 190°, and distils almost without decomposition. It is a diatomic phenol, and is resolved by HCl or HI into CH_3Cl and hexoxydiphenyl.

Cœrulignone, $C_{16}H_{16}O_6 = C_6H_4\left\{\begin{matrix}(OCH_3)_4\\(O—O)\end{matrix}\right.$, separates as a violet powder in the industrial purification of crude wood-vinegar by means of potassium dichromate, and is obtained by the same means from the fraction of beech-tar boiling at 270°. It is insoluble in most solvents, but dissolves in strong sulphuric acid with a fine corn-flower blue colour, changing for a while to red on addition of a large quantity of water; also in phenol, from which it is precipitated by alcohol and ether in slender steel-blue needles. By reduction with tin and hydrochloric acid, it is converted into colourless hydrocœrulignone, $C_{16}H_{18}O_6$, which is reconverted into cœrulignone by oxidation, the two bodies being indeed related to one another in the same manner as quinone and hydroquinone.

Dithymoxyl-trichlorethane,* $CCl_3—CH(C_{10}H_{12}OH)_2$, is formed when sulphuric acid diluted with $\frac{1}{3}$ vol. of glacial acetic acid is added to a cooled mixture of 1 mol. chloral and 2 mol. thymol:

$$CCl_3—CHO + 2C_{10}H_{13}OH = H_2O + CCl_3—CH(C_{10}H_{12}OH)_2.$$

A white precipitate is then formed, the alcoholic solution of which yields the compound in white monoclinic crystals.

Dithymoxyl-trichlorethane is a diatomic phenol, and when treated with C_2H_3OCl or C_7H_5OCl, exchanges its two phenolic hydrogens for acetyl or benzoyl. By strong oxidising agents it is converted into thymoquinone. Heated with zinc-dust, it exchanges its chlorine for hydrogen, forming dithymoxylethane, $C_{22}H_{30}O_2$, part of which is converted, by loss of H_2, into dithymoxylethene, $C_{22}H_{28}O_2$.

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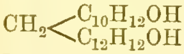
* This compound, and those which follow it, were discovered by Dr. E. Jäger (*Deutsch. Chem. Ges. Ber.* 1874, 1197; Chem. Soc. Jour. 1877, 262), who designates them, not as thymoxyl-compounds, but as thymyl-compounds; but the name "dithymylethane" belongs properly, not to a phenol, but to the hydrocarbon $C_{22}H_{30} = CH_3—CH(C_{10}H_{13})_2$, homologous with diphenyl-ethane and ditolyl-ethane; and so of the rest.

Dithymoxylethane, $CH_3—CH(C_{10}H_{12}OH)_2$, crystallises in rounded plates, melting at 180°, soluble in most of the usual solvents, except water.

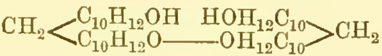
Dithymoxylethene, $CH_2=C(C_{10}H_{12}OH)_2$, forms needle-shaped crystals, melting at 170°–171°, insoluble in water, rather more soluble than the preceding in other solvents. Treated with weak oxidising agents, as with potassium ferrocyanide in dilute alcoholic solution, it forms green crystals, $C_{44}H_{54}O_4$, melting at 214°–215°, soluble in toluene and in chloroform; but if the solution be previously rendered alkaline, a red precipitate is formed, which dissolves in chloroform and separates therefrom in red crystals, melting at 215°, and having the composition $C_{22}H_{26}O_2$.

A mixture of dithymoxylethene and the red crystals dissolved in chloroform deposits, on evaporation, the above-described green needles: $C_{22}H_{28}O_2 + C_{22}H_{26}O_2 = C_{44}H_{54}O_4$. Hence it appears that dithymoxylethene and the two products of its oxidation are related to one another in the same manner as hydroquinone, quinhydrone, and quinone, thus:



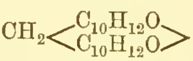
$$CH_2<\begin{array}{l}C_{10}H_{12}OH\\C_{12}H_{12}OH\end{array}$$

Dithymoxylethene.



$$CH_2<\begin{array}{l}C_{10}H_{12}OH \quad HOH_{12}C_{10}\\C_{10}H_{12}O——OH_{12}C_{10}\end{array}>CH_2$$

Dithymoxyl-quinhydronethene.



$$CH_2<\begin{array}{l}C_{10}H_{12}O\\C_{10}H_{12}O\end{array}>$$

Dithymoxyl-quinonethene.

Alcohols.

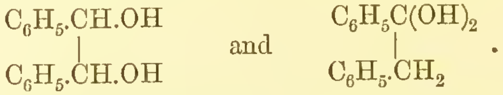
Benzhydrol, $C_{13}H_{12}O = C_6H_5—CH(OH)—C_6H_5$, is obtained by the action of sodium-amalgam on a solution of benzophenone in dilute alcohol. It crystallises in needles, melts at 68°, and boils at 298°, with partial decomposition into water and benzhydrolic ether, $[(C_6H_5)_2CH]_2O$.

Toluylene Hydrate or **Stilbene Hydrate**, $C_{14}H_{14}O = C_6H_5.CH_2.CH(OH).C_6H_5$, is formed by the action of sodium-amalgam on deoxybenzoïn, $C_{14}H_{12}O$ (p. 571), and by heating deoxybenzoïn or hydrobenzoïn with alcoholic potash. Long, slender, brittle needles, having a vitreous lustre melting at 62°; insoluble in water, easily soluble in alcohol and ether. Resolved by boiling with dilute sulphuric acid into stilbene and water; oxidised by nitric acid to deoxybenzoïn; reduced by HI to dibenzyl. With acetyl chloride, it forms toluylene acetate, $C_{14}H_{13}.O.C_2H_3O$, which is a viscid liquid.

Dimethyl-benzhydrol, $C_{15}H_{16}O = CHOH(C_6H_4.CH_3)_2$, obtained by the action of sodium-amalgam on ditolylketone in alcoholic solution forms slender needles melting at 69°.

Triphenyl-carbinol, $C_{19}H_{16}O=(C_6H_5)_3C(OH)$, from triphenyl-methane by oxidation with chromic acid mixture, forms monoclinic crystals, melts at 157°, boils without decomposition above 360°. Its solution in benzene heated with P_2O_5 yields triphenyl-methane and dibenzyl.

Tolylene Glycols, $C_{14}H_{14}O_2$.—Two diatomic alcohols of this composition, called Hydrobenzoïn and Isohydrobenzoïn, are formed by the action of zinc and hydrochloric acid on benzaldehyde; also by that of sodium-amalgam on the same compound in alcoholic solution. By oxidation with chromic acid mixture both of them are converted into benzaldehyde and benzoic acid: consequently they must be represented by the formulæ:

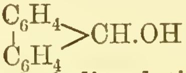


$$\begin{array}{c} C_6H_5.CH.OH \\ | \\ C_6H_5.CH.OH \end{array} \quad \text{and} \quad \begin{array}{c} C_6H_5C(OH)_2 \\ | \\ C_6H_5.CH_2 \end{array} .$$

Now one of them (hydrobenzoïn) is the sole product of the action of sodium-amalgam on benzil, $C_6H_5—CO—CO—C_6H_5$: this, therefore, must be represented by the left hand or symmetrical formula; and isohydrobenzoïn, if not a mere physical modification, by the unsymmetrical formula. By the action of PBr_5, both compounds are converted into tolylene dibromide, $C_7H_6Br_2$.

Hydrobenzoïn is sparingly soluble in water, easily in alcohol, and crystallises in large rhombic plates, melting at 132·5°, and subliming without decomposition. By heating with strong nitric acid it is converted into benzoïn. Its acetylic ether, $C_{14}H_{12}(OC_2H_3O)_2$, forms large prisms melting at 133°–134°.

Isohydrobenzoïn crystallises from water in long, shining, four-sided hydrated prisms, which effloresce on exposure to the air; from alcohol in anhydrous monoclinic prisms. It melts at 119·5°, is more soluble in alcohol then hydrobenzoïn; is not converted into benzoïn by nitric acid.

Fluorenyl Alcohol, $C_{13}H_{10}O=$  $\begin{array}{c} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CH.OH$, produced by the action of sodium-amalgam on an alcoholic solution of diphenylene ketone, forms colourless hexagonal laminæ, melting at 153°.

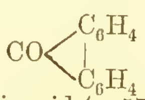
Ketones.

Diphenyl Ketone or **Benzophenone,** $C_6H_5.CO.C_6H_5$, is formed by oxidation of diphenyl-methane and diphenyl-ethane (p. 564) with chromic acid mixture; by heating mercury-diphenyl (p. 459) with benzoyl chloride; and most readily (together with benzene) by distillation of calcium benzoate. It usually crystallises in large rhombic prisms melting at 48°–49°, sometimes also in rhombohedrons melting at 27°; the latter modification is converted on standing into the former. It has an aromatic odour, boils at 295°, dissolves easily in alcohol. Treated with PCl_5, it is converted into benzophenonic chloride, $(C_6H_5)_2CCl_2$, a liquid boiling at about 300°. Sodium amalgam converts it into benzhydrol (p. 569).

Phenyl-tolyl Ketone, $C_{14}H_{12}O = C_6H_5.CO.C_6H_4(CH_3)$, is obtained in two modifications by oxidation of benzyl-toluene; by heating a mixture of benzoic acid and toluene with P_2O_5; by heating a mixture of calcium benzoate and paratoluate; and by heating benzyl chloride and toluene with zinc-dust. The α-compound (para) exists in two dimorphous modifications—one, hexagonal, melting at 55°; the other, monoclinic, melting at 59°–60°. Boiling point, 310°–312°. Heated with soda-lime it yields benzene and paratoluic acid. The β-compound, which is liquid, has not been obtained pure. By distillation with zinc-dust, it yields anthracene; with lead oxide, anthraquinone: the α-compound does not yield these products.

Ditolyl Ketone, $CO(C_6H_4.CH_3)_2$, forms rhombic crystals melting at 95°.

Dibenzyl Ketone, $CO(CH_2.C_6H_5)_2$, obtained by distillation of calcium α-toluate, forms colourless crystals, m. p. 30°, b. p. 320°–321°; yields by oxidation benzoic and carbonic acids.



Diphenylene Ketone, $C_{13}H_8O = CO\left\langle\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right.$, obtained by heating diphenic acid or phenyl-benzoic acid (p. 572) with lime, also by oxidising fluorene with chromic acid mixture, forms large yellow rhombic crystals, melts at 84°, boils at 336°–338°; is converted by reducing agents into fluorene, by fusion with potash into phenyl-benzoic acid.

Benzoin, $C_{14}H_{12}O_2 = C_6H_5.CO.CH(OH).C_6H_5$, formed by heating hydrobenzoïn with nitric acid (specific gravity 1·4), and by mixing bitter almond oil with a concentrated alcoholic solution of potassium cyanide, crystallises in shining prisms melting at 133°–134°; dissolves sparingly in water and in cold alcohol or ether, freely in hot alcohol. Converted by chromic acid mixture into benzaldehyde and benzoic acid; by heating with fuming hydriodic acid into dibenzyl; by heating with alcoholic potash, into hydrobenzoïn and benzile, together with benzylic acid, benzoic acid, and other products:

$$\underset{\text{Benzoïn.}}{2C_{14}H_{12}O_2} = \underset{\text{Hydrobenzoïn.}}{C_{14}H_{14}O_2} + \underset{\text{Benzile.}}{C_{14}H_{10}O_2}.$$

With acetyl chloride it yields acetyl-benzoïn, $C_{14}H_{11}(C_2H_3O)O_2$, which forms crystals melting at 75°.

Deoxybenzoin or **Phenyl-benzyl Ketone,** $C_{14}H_{12}O = C_6H_5.CO.CH_2(C_6H_5)$, is formed by the action of zinc and hydrochloric acid on benzoïn and chlorobenzile (p. 572); by heating monobromostilbene with water to 180°–190°, and by distillation of a mixture of benzoate and α-toluate of calcium :

$$C_6H_5.CO.OH + C_6H_5.CH_2.CO.OH = CO_2 + H_2O + C_6H_5.CO.CH_2C_6H_5 .$$

It crystallises from alcohol in large plates melting at 55° ; sublimes without decomposition ; is converted by sodium-amalgam into toluylene hydrate (p. 569), by PCl_5 into monochlorotoluylene, and by heating with hydriodic acid into benzile.

Benzile, $C_{14}H_{10}O_2 = C_6H_5CO.CO.C_6H_5$ (*Dibenzoyl*), is formed by oxidation of benzoïn with nitric acid or chlorine ; and, together with stilbene, by heating stilbene bromide with water and silver oxide. It crystallises in large six-sided prisms, melting at 90°, insoluble in water, soluble in alcohol and ether. By oxidation with chromic acid mixture, it is converted into benzoic acid; by nascent hydrogen (zinc and HCl, or iron filings and acetic acid) into benzoïn ; by heating with PCl_5 into benzile chloride, $C_{14}H_{10}Cl_2O$ or $C_6H_5.CCl_2.CO.C_6H_5$, which crystallises in rhombic prisms melting at 71°, and is converted by zinc and HCl into deoxybenzoïn. Benzile and its chloride, heated to 200° with PCl_5 yield tolane tetrachloride, $C_{14}H_{10}Cl_4$.

Acids.

Diphenylcarbonic Acid, $C_{13}H_{10}O_2 = C_6H_5.C_6H_4.CO_2H$ (1 : 4), is produced by heating cyanodiphenyl, $C_{12}H_9(CN)$, with alcoholic potash (p. 562), or by oxidising diphenyl-benzene (p. 566) dissolved in glacial acetic acid with chromic anhydride. It crystallises from alcohol in tufts of needles ; melts at 218°–219° ; is converted by heating with lime into diphenyl, and by oxidation with chromic acid into terephthalic acid.

Phenyl-benzoic acid, $C_{13}H_{10}O_2 = C_6H_5.C_6H_4.CO_2H$ (? 1:2), produced by the action of melting potash on diphenylene ketone (p. 571) forms ramified crystals, melting at 110°–111° ; reconverted into diphenylene ketone by heating with lime.

Diphenyl-dicarbonic Acid, $C_{14}H_{10}O_4 = C_{12}H_8(CO_2H)_2$ (*para*), from dicyanodiphenyl, $C_{12}H_8(CN)_2$, is a white amorphous powder, insoluble in alcohol and ether, neither fusible nor sublimable. Heated with lime it yields diphenyl. Its barium and calcium salts are nearly insoluble in water. The diethylic ether melts at 112°.

Diphenic acid, isomeric with the last, is formed by oxidation of phenanthrene or phenanthrene-quinone with chromic acid mixture. It melts at 226°, sublimes in needles, dissolves very easily in alcohol and ether. The barium and calcium salts are easily soluble in water ; the diethylic ether is liquid.

Diphenylacetic Acid, $C_{14}H_{12}O_2 = (C_6H_5)_2CH.CO.OH$, is formed by heating benzilic acid with hydriodic acid to 150°, and by heating a mixture of phenyl-bromacetic acid and benzene with zinc-dust:

$$C_6H_5.CHBr.CO_2H + C_6H_6 = HBr + (C_6H_5)_2CH.CO_2H.$$

It crystallises from water in slender needles, from alcohol in laminæ, and melts at 146°; is converted by chromic acid mixture into diphenyl ketone; by heating with soda-lime into diphenyl-methane.

Diphenyl-glycollic or **Benzilic Acid,** $C_{14}H_{12}O_3 = (C_6H_5)_2C(OH).CO_2H$, is formed by passing bromine-vapour into diphenyl-acetic acid, and boiling the product with water; also by heating benzile with alcoholic potash (not in excess); in this reaction, a transposition of atoms must take place. It crystallises in shining needles or prisms, easily soluble in hot water and in alcohol; melts at 150°, turning red at the same time. It dissolves with dark red colour in sulphuric acid. By heating with HI, it is converted into diphenyl-acetic acid; by oxidation into diphenyl ketone; by distillation of its barium salts into benzhydrol (p. 569).

Benzoyl-benzoic Acids, $C_{14}H_{10}O_3 = C_6H_5.CO.C_6H_4.CO_2H$.—The *para*-modification is formed by oxidation of solid phenyl-tolyl ketone, *para*-benzyl-benzoic acid, benzyl-toluene, benzylethyl-benzene, and ethylbenzyl-toluene (p. 565), with chromic acid mixture. It sublimes in laminæ, resembling benzoic acid, and melts at 194°. The *ortho*-modification, from liquid phenyl-tolyl ketone, crystallises from hot water in needles or prisms containing $1H_2O$, The crystals melt at 85°–87°; the anhydrous acid at 127°–128°.

Benzhydryl-benzoic acids, $C_6H_5.CH.(OH).C_6H_4.CO_2H$.—The *para*-acid, formed by the action of nascent hydrogen on *para*-benzyl-benzoic acid, crystallises in needles, melts at 164°–165°, and is reconverted by oxidation into *para*-benzoylbenzoic acid. The *ortho*-acid cannot be obtained in the free state, as on attempting to prepare it by the action of nascent hydrogen on *ortho*-benzylbenzoic acid, it splits up into water and the anhydride $C_{14}H_{10}O_2$. This compound crystallises from alcohol or ether in prisms melting at 115°; is converted by oxidation into *ortho*-benzylbenzoic acid, and by PCl_5 into anthraquinone and chlorinated compounds.

Benzyl-benzoic acid, $C_{14}H_{12}O_2 = C_6H_5.CH_2.C_6H_4.CO_2H$.—The *para*-acid is obtained by the prolonged action of HI and phosphorus at 160°–170° on *para*-benzoyl- or benzhydryl-benzoic acid. Laminæ or needles, melting at 157°. The *ortho*-acid obtained in like manner from *ortho*-benzoyl-benzoic acid, forms slender shining needles, melting at 114°.

NAPHTHALENE GROUP.

Naphthalene, $C_{10}H_8$.—This hydrocarbon is produced in the decomposition of toluene, xylene, and cumene at a red heat (p. 428); also by passing vapour of benzene, cinnamene, chrysene, or anthracene through a red-hot tube. It is formed in large quantities as a bye-product in the preparation of coal-gas, its production doubtless arising from reactions similar to those just mentioned. When the last portion of the volatile oily product which passes over in the distillation of coal-tar is collected apart and left to stand, a quantity of solid crystalline matter separates, which is principally naphthalene. An additional quantity may be obtained by pushing the distillation until the contents of the vessel begin to char: the naphthalene then condenses in the solid state, but dark-coloured and very impure. By simple sublimation, once or twice repeated, it is obtained perfectly white.

Naphthalene is formed synthetically from phenyl-butylene, $C_6H_5.CH_2.CH_2.CH{=}CH_2$, which is obtained by the action of sodium on a mixture of benzyl chloride, $C_6H_5.CH_2Cl$, and allyl iodide, $CH_2I.CH{=}CH_2$. This hydrocarbon or its bromide passed through a red-hot tube filled with lime, is resolved into naphthalene and hydrogen, $C_{10}H_{12} = C_{10}H_8 + 2H_2$. Naphthalene forms large colourless, transparent, brilliant, crystalline plates, exhaling a faint and peculiar odour. It melts at 79·2° to a clear, colourless liquid, which crystallises on cooling; boils at 218°. When strongly heated in the air, it takes fire, and burns with a red and very smoky flame. It is insoluble in cold water, but soluble to a slight degree at the boiling heat; alcohol and ether dissolve it easily; a hot saturated alcoholic solution deposits fine iridescent crystals on cooling. It unites with *picric acid*, forming the compound $C_{10}H_8.C_6H_3(NO_2)_3O$, which crystallises in stellate groups of needles.

Naphthalene, like benzene and its homologues, forms addition-products with hydrogen and chlorine. Heated with PH_4I to 190°, or with HI and amorphous phosphorus to 220°–250°, it forms the tetrahydride, $C_{10}H_8.H_4$, a pungent liquid boiling at 205°. With chlorine, it forms the compound, $C_{10}H_8.Cl_2$, which is a pale yellow oil, and $C_{10}H_8.Cl_4$, $C_{10}H_7Cl.Cl_4$, and $C_{10}H_6Cl_2.Cl_4$, which crystallise in monoclinic prisms, melting respectively at 182°, 128°–130°, and 172°.

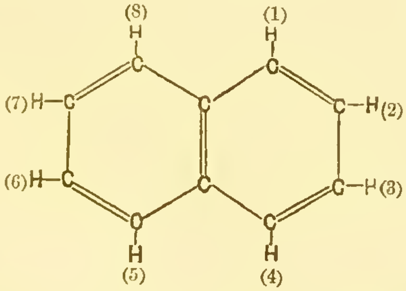
The structure of the naphthalene molecule is deduced by Graebe (Liebig's *Annalen*, cxlix. 26) from the following considerations. Naphthalene is converted by oxidation into phthalic or benzene-dicarbonic acid, $C_6H_4(CO_2H)_2$, two of its carbon-atoms being removed as carbon dioxide, while two others remain in the form of carboxyl:

$$C_{10}H_8 + O_0 = C_6H_4(CO_2H)_2 + 2CO_2 + H_2O.$$

Hence naphthalene contains a benzene-residue, C_6H_4, and may by represented by the formula $C_6H_4.C_4H_4$. The same conclusion follows from the synthesis of naphthalene from phenyl-butylene. But phthalic acid is likewise produced by oxidation of dichloronaphthoquinone, $C_{10}H_4Cl_2O_2$: consequently, this compound has its two chlorine-atoms and two oxygen-atoms associated with the four carbon-atoms which undergo oxidation, and may be represented by the formula $C_6H_4.C_4Cl_2O_2$. By the action of phosphorus pentachloride, the two oxygen-atoms are replaced by two chlorine-atoms, and at the same time one of the four hydrogen-atoms is replaced by chlorine, the result being pentachloronaphthalene, $C_6H_3Cl(C_4Cl_4)$, which is converted by oxidation into tetrachlorophthalic acid, $C_6Cl_4(CO_2H)_2$. In this reaction, therefore, two of the carbon-atoms belonging to the left-hand group in the molecule $C_6H_3Cl(C_4Cl_4)$ are removed as carbon dioxide, while two others yield the two groups CO_2H, and the remaining two, together with the four standing on the right, form the benzene nucleus C_6Cl_4 of tetrachlorophthalic acid.

These transformations show that the molecule of naphthalene is symmetrical, and composed of two benzene-nuclei united in the manner represented by the following figure :

Fig. 19.



The replacement of the hydrogen-atoms in naphthalene by other elements and by compound radicles gives rise to numerous substitution-derivatives, which are obtained by methods similar to those by which the benzene-derivatives are produced. The number of possible isomerides among the naphthalene derivatives is, however, much greater than those of the benzene-derivatives. Thus the mono-derivatives of benzene do not admit of isomeric modifications, but in naphthalene the places 1, 4, 5, 8 (see the preceding figure), though similar to each other, are different from the places 2, 3, 6, 7, which are likewise similar amongst themselves. Hence there will be two modifications of each mono-derivative of naphthalene (chloro-, nitro-, &c.). Those modifications in which the substituted radicles occupies the place 1 (= 4, 5, or 8), are called α-derivatives; those in which it is placed at 2, 3, 5, or 7, are called β-derivatives. The di-derivatives, $C_{10}H_8X_2$, exhibit ten isomeric modifications, according as the substituted radicles are situated : (1) in the same benzene-ring (1:2, 1:3, 1:4, or 5:6, 5:7, 5:8, and 2:3, or 6:7); secondly, in different rings (1:5, 1:6, 1:7, 1:8, 2:6, and 2:7). The list of actually known modifications is, however, very incomplete.*

Chloronaphthalenes are obtained by boiling the chlorides of naphthalene with alcoholic potash, which removes HCl; these, when subjected to the action of chlorine, also form addition-products such as $C_6H_7Cl.Cl_2$; and from these, by the action of alcoholic potash, more highly chlorinated substitution-derivatives may be obtained.

Monochloronaphthalenes, $C_{10}H_7Cl$. — α, from naphthalene dichloride is a liquid boiling at 250°. — β. By the action of PCl_5 on β-naphthol. Colourless crystalline mass, m. p. 60°; b. p. 256°–258°.

$C_{10}H_6Cl_2$ is known in seven, and $C_{10}H_5Cl_3$, in four modifications. $C_{10}Cl_8$, the final product of the action of chlorine on naphthalene, forms prisms melting at 135°.

Of monobromonaphthalene, two modifications are known, one formed by direct bromination, being a liquid boiling at 277°; the other from β-naphthylamine by the diazo-reaction with alcohol, forming white shining laminæ, melting at 68°.

Iodonaphthalene, $C_{10}H_7I$, produced by the action of iodine on mercuric naphthide, is an oil boiling at 300°.

Cyanonaphthalenes, or Naphthyl Cyanides, $C_{10}H_7.CN$ (α and β) are formed by distilling the potassium salts of the corresponding naphthalenesulphonic acids with potassium cyanide.— α. Crystallises in needles, melts at 37·5°, and boils at 297°–298°.— β. Forms laminæ, melts at 66·5°, boils at 304°–305°.

Dicyanonaphthalenes, $C_{10}H_6(CN)_2$ are formed in like manner from the naphthalene-disulphonic acids.—α. Needles melting at 267°–268°.—β. Needles melting at 296°–297°.

Nitrosonaphthalene, $C_{10}H_7.NO$, is formed by the action of nitrogen oxybromide, NOBr (solution of NO and Br in CS_2 at $-20°$) on mercuric naphthide:

$$(C_{10}H_7)_2Hg + NOBr = C_{10}H_7.NO + C_{10}H_7.Hg.Br.$$

It separates from solution in benzene or light petroleum in yellow nodules, turning red in contact with the air; melts at 85°, and decomposes at 134°. Its solution in phenol is coloured blue by sulphuric acid.

Nitronaphthalene, $C_{10}H_7.NO_2$, obtained by heating a solution of naphthalene in glacial acetic acid with ordinary nitric acid for half an hour, crystallises from alcohol in sulphur-yellow prisms, melts at 61°, boils at 304°; insoluble in alcohol, ether, and carbon sulphide.

Two dinitronaphthalenes are obtained by boiling naphthalene or mononitronaphthalene with nitric acid till the oily liquid which floats on the surface has disappeared.—α. Colourless prisms melting at 213°.—β. Rhombic plates melting at 170°.

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* For the latest researches on naphthalene-derivatives, see Liebermann (Liebig's *Annalen*, clxxxiii. 225), and Atterberg (*Deutsch. Chem. Ges. Ber.*, 1876, pp. 1730, 1734).

These compounds, boiled with fuming nitric acid, yield three trinitronaphthalenes, boiling respectively at 122°, 147°, and 218°; and on further boiling, two tetranitronaphthalenes, melting at 200° and 259°.

Amidonaphthalenes or **Naphthylamines**, $C_{10}H_7.NH_2$.—The α-modification obtained by reduction of nitronaphthalene, crystallises in needles or prisms, easily soluble in alcohol; has a pungent odour; melts at 50°, and boils at 300°. It forms easily soluble crystalline salts, the solutions of which give with chromic acid or ferric chloride, a blue precipitate, quickly changing to a purple-red powder of *oxynaphthylamine*, $C_{10}H_9NO$. α-Naphthylamine, heated with glacial acetic acid, yields *α-Acetonaphthalide*, $C_{10}H_7.NH(C_2H_3O)$, which crystallises in fine silky fibres, melting at 159°.

β-Naphthylamine is obtained from bromonitronaphthylamine, which is formed by nitration of bromacetonaphthalide, $C_{10}H_6Br.NH.C_2H_3O$. The amido-group is eliminated by the action of nitrous acid and alcohol, and the resulting bromonitronaphthalene is reduced by tin and hydrochloric acid. β-Naphthylamine forms nacreous laminæ melting at 112°.

Nitronaphthylamine, $C_{10}H_6NO_2.NH_2$, obtained by reduction of α-dinitronaphthalene, forms small red crystals melting at 118°–119°. Two isomeric nitronaphthylamines melting at 191° and 158°–159° are formed by the nitration of the acetyl-compound, which melts at 159°.

Diamidonaphthalene or Naphthylenediamine, from nitronaphthylamine (m. p. 191°), is converted by oxidation with dilute chromic acid into naphthoquinone. Two other naphthylenediamines are obtained by reduction of dinitronaphthalenes.

The naphthylamines treated with nitrous acid yield diazo-compounds, analogous to those obtained from aniline.

Diazo-amidonaphthalene, $C_{20}H_{15}N_3 = C_{10}H_7.N_2.NH(C_{10}H_7)$, obtained by the action of nitrous acid on a cold alcoholic solution of naphthylamine, forms brown laminæ, and is resolved by heating with acids into naphthylamine and naphthol:

$$C_{10}H_7.N_2.NH.C_{10}H_7 + H_2O = C_{10}H_7.OH + C_{10}H_7.NH_2 + N_2.$$

The action of nitrous acid on a warm alcoholic solution of naphthylamine, or of potassium nitrite on its solution in hydrochloric acid, produces amidazonaphthalene, $C_{10}H_7.N_2.C_{10}H_6.NH_2$, metameric with diazo-amidonaphthalene, and analogous to amidazobenzene (p. 467). It dissolves easily in alcohol, and crystallises in orange-red needles having a green metallic lustre. Its salts are violet-coloured. Heated with naphthylamine it forms a base, $C_{30}H_{21}N_3$, analogous to rosaniline:

$$C_{20}H_{15}N_3 + C_{10}H_0N = NH_3 + C_{30}H_{21}N_3.$$

The hydrochloride of this base, $C_{30}H_{21}N_3.HCl + H_2O$, forms the fine red dye-stuff called *Naphthalene-red* or *Magdala-red*. It crystallises in green metallically lustrous needles, and dissolves in alcohol, forming a red solution, which when dilute exhibits a beautiful fluorescence.

Mercuric Naphthide, $(C_{10}H_7)_2Hg$, produced by the action of sodium-amalgam on a solution of bromonaphthalene in benzene, forms shining crystals, easily soluble in hot benzene, sparingly in alcohol and ether. It melts at 243°, and decomposes partially when sublimed. Haloïd acids decompose it into naphthalene and mercury-salts. It unites with iodine, forming the compound $(C_{10}H_7)_2HgI_2$, which is decomposed by a larger quantity of iodine, thus:

$$(C_{10}H_7)_2HgI_2 + I_2 = HgI_2 + 2C_{10}H_7I.$$

Heated with soda-lime it yields dinaphthyl and naphthalene.

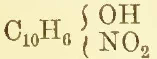
Naphthalene-sulphonic Acids, $C_{16}H_7.SO_3H$, α and β, are formed by gradually heating naphthalene with sulphuric acid, and may be separated by fractional crystallisation of their barium or lead-salts, those of the α-acid being much more soluble in water and alcohol than the β-salts. The free acids are crystalline and deliquescent. The α-acid is converted by heat into the β-acid; the latter is therefore almost the sole product obtained at a high temperature (160°). The α-acid, heated with dilute hydrochloric acid to 200°, is resolved into naphthalene and sulphuric acid. The *chlorides*, $C_{10}H_7.SO_2Cl$, are obtained by heating the potassium salts with PCl_5. They crystallise in shining laminæ, α more soluble in ether than β. The α-chloride melts at 66°; β at 76°. By zinc and sulphuric acid they are converted into *mercaptans*, $C_{10}H_7.SH$.

By prolonged heating of naphthalene with sulphuric acid, two *naphthalene-disulphonic acids*, $C_{10}H_6(SO_3H)_2$, are formed, which when distilled with KCy yield the corresponding *dicyanides*, $C_{10}H_6(CN)_2$.

Naphthols, $C_{10}H_7.OH$, are formed by fusing the two mono-sulphonic acids with potash.

α-Naphthol is also produced by boiling the aqueous solution of diazonaphthalene nitrate (from α-naphthylamine) with nitrous acid. It crystallises in colourless monoclinic prisms, melts at 94°, boils at 278°–280°; is nearly insoluble in cold water, somewhat more soluble in hot water, easily in alcohol and ether. Ferric chloride and bleaching powder give to the aqueous solution a transient violet colour.

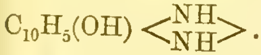
With alkalis, &c., α-naphthol forms derivatives exactly like those of phenol. The *ethylic ether*, $C_{10}H_7.O.C_2H_5$, is a colourless liquid, boiling at 272°, not solidifying at −5°. *α-Acetyl-naphthol*, $C_{10}H_7.O.C_2H_3O$, formed by the action of acetyl chloride, is a yellowish liquid, insoluble in water. The *benzoyl* derivative melts at 56°.

Nitro-α-naphthol,  $C_{10}H_6\left\{\begin{matrix}OH\\NO_2\end{matrix}\right.$ (1 : 4) obtained by boiling nitro-naphthylamine (m. p. 191°) with potash, crystallises from alcohol in lemon-yellow capillary needles; from acetic acid or acetone in golden-yellow prisms; melts at 164°. Its sodium salt is a yellow dye-stuff called *Campobello yellow*. By reduction with tin and HCl, it yields amido-α-naphthol, which, by boiling with bromine-water or by the action of nitrous acid, is converted into naphthoquinone.

An isomeric nitro-α-naphthol, formed from the nitronaphthylamine melting at 158°–159°, crystallises in greenish-yellow laminæ, melting at 128°, much less soluble in alcohol than the preceding.

Dinitro-α-naphthol, $C_{10}H_5(NO_2)_2OH$, is formed by mixing α-naphthylamine with 4–6 parts of strong nitric acid; by boiling diazonaphthalene hydrochloride with nitric acid; or by gently heating a solution of α-naphthalene-sulphonic acid with nitric acid. Shining sulphur-yellow crystals, melting at 138°, sparingly soluble in alcohol and ether, more freely in chloroform. It forms salts with bases, and decomposes carbonates. Its calcium and sodium salts form splendid yellow dyes, known as naphthalene-yellows.

Dinitronaphthol treated with zinc and hydrochloric acid yields the hydrochloride of *diamidonaphthol*, $C_{10}H_5(NH_2)_2.OH$, the aqueous solution of which is converted by exposure to the air, or by the action of ferric chloride, into the hydrochloride of *di-imidonaphthol*,



$$C_{10}H_5(OH) \left< \begin{matrix} NH \\ NH \end{matrix} \right> .$$

β-Naphthol or Isonaphthol, $C_{10}H_7.OH$, from β-naphthalene-sulphonic acid, crystallises in small rhombic tables, melts at 122°, boils at 285°–290°, and sublimes with great facility; dissolves sparingly in boiling water, easily in alcohol and ether. The *ethylic ether*, $C_{10}H_7.O.C_2H_5$, melts at 33°, the acetyl-compound at 60°, the benzyl-compound at 107°.

Dinitro-β-naphthol, obtained by heating the alcoholic solution of β-naphthol with dilute nitric acid, forms yellow needles melting at 195°.

Dioxynaphthalene or *Naphthohydroquinone*, $C_{10}H_6(OH)_2$ (1 : 4), is formed from naphthoquinone by heating with hydriodic acid and amorphous phosphorus. It crystallises from hot water in long colourless needles, melting at 176°, converted by oxidation into naphthoquinone. An isomeric compound, obtained from naphthalene-disulphonic acid, forms needles slightly soluble in water.

Naphthoquinone, $C_{10}H_6 \left< \begin{matrix} O \\ O \end{matrix} \right>$, is formed by oxidation of naphthalene with chromic anhydride dissolved in glacial acetic acid; more readily by adding a dilute aqueous solution of chromic acid to a solution of diamido-naphthalene hydrochloride (p. 577); on distilling the liquid, the naphthoquinone passes over with the steam. Large sulphur-yellow triclinic tables, having a pungent odour, melting at 125°, subliming below 100°; insoluble in cold water, slightly soluble in cold alcohol, easily in hot alcohol and in ether. Converted by oxidation with nitric acid into phthalic acid.

Dichloronaphthoquinone, $C_{10}H_4Cl_2O_2$, is formed by heating α-naphthol or dinitronaphthol (commercial naphthalene yellow) with potassium chlorate and hydrochloric acid; also by the action of chromyl chloride, CrO_2Cl_2 on a solution of naphthalene in glacial acetic acid. Crystallises in golden-yellow needles melting at 189°; oxidised by nitric acid to phthalic acid; converted by PCl_5 into $C_{10}H_3Cl_5$, which oxidises to chlorophthalic acid. Boiled with soda-ley, it dissolves with red colour, forming the sodium salt of chloronaphthalic acid, $C_{10}H_4Cl(O_2)OH$, which crystallises in yellow needles, melting at 200°.

Oxynaphthoquinone or *Naphthalenic acid*, $C_{10}H_5(OH<{O \atop O}>$, is formed from the hydrochloride of di-imidonaphthol (p. 579) by heating with dilute hydrochloric acid to 120°:

$$C_{10}H_5(N_2H_2)OH + 2H_2O = 2NH_3 + C_{10}H_5(O_2)OH.$$

Light yellow, strongly electric powder, or yellow needles; sparingly soluble in hot water, easily in alcohol and ether; unites with nascent hydrogen, forming trioxynaphthalene. It is a rather strong monobasic acid, capable of decomposing carbonates. Its alkali-salts are blood-red, and easily soluble in water.

Dioxynaphthoquinone or *Naphthazarin*, $C_{10}H_4(O_2)(OH)_2$.—This compound is a dye-stuff very much like alizarin. It is obtained by gradually adding dinitronaphthol (4 parts), and granulated zinc ($\frac{1}{2}$ – 1 part), to a mixture of strong sulphuric acid (40 parts), and fuming sulphuric acid (4 parts) heated to 200° (not above 205°). On diluting the mixture with water, boiling, and filtering, the naphthazarin separates as a red gelatinous mass, which may be purified by sublimation. Long needles having a splendid green metallic lustre, dissolving in alcohol with red, in ammonia with sky-blue colour. The solutions give violet-blue precipitates with baryta- and lime-water, crimson with alum.

Naphthoic Acids, $C_{10}H_7.CO_2H$.—α-Naphthoic acid is obtained from α-cyanonaphthalene (p. 576); also by fusing potassium α-naphthalenesulphonate with sodium formate, and by the action of sodium-amalgam on a mixture of bromonaphthalene and ethyl chlorocarbonate. Slender needles melting at 160°; slightly soluble in hot water, easily in hot alcohol. By distillation with baryta it is resolved into naphthalene and carbon dioxide. Its *ethylic ether* boils at 309°; the *chloride*, $C_{10}H_7COCl$ at 297°.

β-Naphthoic or *Isonaphthoic acid*, from β-cyanonaphthalene, crystallises from hot water in long silky needles melting at 182°.

Oxynaphthoic acids, $C_{10}H_6<{OH \atop CO_2H}$, are formed from the two naphthols by the action of sodium and carbon dioxide. The α-acid melts at 185°, and forms solutions which are coloured blue by ferric chloride. The β-acid is difficult to prepare.

Naphthalene-dicarbonic acids, $C_{10}H_6(CO_2H)_2$.—Of these acids there are three known modifications. Two of them, α and β, are obtained by heating the corresponding dicyanonaphthalenes with strong hydrochloric acid to 200°–210°.—α. Forms long pointed needles, melting, with decomposition, above 300°; its salts, except those of the alkalis, are but slightly soluble in water. The β-acid is very much like the α-acid, except that it crystallises in short slender needles.

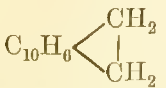
The third modification, *naphthalic acid*, obtained by oxidation of acenaphthene and acenaphthylene with chromic acid mixture, forms slender needles, and decomposes at 140°–150°, without melting, into water and the anhydride, $C_{12}H_6O_3$, which melts at 266°. The acid is nearly insoluble in water. Its calcium salt heated with lime yields naphthalene. The *methylic ether*, $C_{10}H_6(CO_2CH_3)_2$, crystallises in prisms melting at 102°–103°.

Dinaphthyl, $C_{20}H_{14} = C_{10}H_7.C_{10}H_7$, is formed by the action of sodium on monobromonaphthalene; by oxidation of naphthalene with MnO_2 and sulphuric acid; and by heating mercuric naphthide with soda-lime (p. 578). Colourless laminæ, with a mother-of-pearl lustre; slightly soluble in cold alcohol, easily in ether; melts at 154°, and sublimes without decomposition. By further oxidation with MnO_2 and sulphuric acid it is converted, like naphthalene, into phthalic acid.

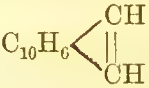
Three *isodinaphthyls* are obtained by passing naphthalene-vapour alone, or mixed with antimony trichloride, through a red-hot tube, and may be separated by repeated crystallisation from petroleum; melting points, 187°, 147°, and 75°.

Dinaphthylmethane, $C_{21}H_{16} = C_{10}H_7.CH_2.C_{10}H_7$, obtained (like diphenyl-methane, p. 564) by the action of sulphuric acid on a mixture of naphthalene and methylal diluted with chloroform, crystallises in short prisms, melts at 109°, boils at a temperature above 360°, and may be distilled without decomposition. With picric acid it forms the compound $C_{20}H_{16}.2C_6H_3(NO_2)_3O$, which crystallises in reddish yellow prisms.

Homologues of Naphthalene are obtained by the action of sodium on a mixture of bromonaphthalene and alcoholic bromides dissolved in ether; and these, when passed through red-hot tubes, split up into hydrogen and unsaturated hydrocarbons. *Methyl-naphthalene*, $C_{10}H_7.CH_3$, is a thick liquid, boiling at 232°, not solidifying at −18°; *ethyl-naphthalene*, $C_{10}H_7.C_2H_5$, boils at 251°–252°, and does not solidify at −14°.

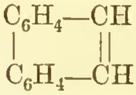
Acenaphthene, $C_{12}H_{10}$ = 

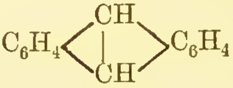
$C_{10}H_6\left\langle\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\right.$, is formed by passing ethyl-naphthalene through a red-hot tube, and occurs in the portion of coal-tar oil boiling at 250°–260°, from which it may be separated by cooling. It crystallises from fusion in flat prisms, from alcohol in long needles; melts at 95°; boils at 277·5°; forms with picric acid the compound $C_{12}H_{10}.C_6H_2(NO_2)_3OH$, which crystallises from alcohol in long needles melting at 161°–162°. By oxidation with chromic acid mixture, acenaphthene is converted into naphthalic acid (p. 581).

Acenaphthylene, $C_{12}H_8$ =  $C_{10}H_6<\begin{matrix}CH\\ \|\\ CH\end{matrix}$, is formed by passing the vapour of acenaphthene over gently heated lead-oxide. It dissolves easily in alcohol, crystallises in yellow tables, sublimes at ordinary temperatures, melts at 92°–93°, and boils, with partial decomposition, at about 265°–275°. Its picric acid compound forms yellow needles melting at 202°. By chromic acid mixture it is oxidised to naphthalic acid. Its dibromide, $C_{10}H_8Br_2$, melts at 122°.

PHENANTHRENE AND ANTHRACENE GROUP.

Tha primary compounds of this group are two isomeric solid hydrocarbons, $C_{14}H_{10}$, occurring in the portion of coal-tar which boils between 320° and 360°. They are nearly related to benzene, and their modes of formation and decomposition show that their structure may be very probably represented by the following formulæ:


Phenanthrene.


Anthracene.

Both consist of two benzene residues united by the group C_2H_2; but in phenanthrene the two benzene-groups are joined directly, in the same manner as in diphenyl, whereas in anthracene they are united only through the medium of the group =CH—CH=.

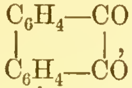
Phenanthrene, $C_{14}H_{10}$, may be formed by abstraction of hydrogen from dibenzyl, $C_{14}H_{14}$, and stilbene, $C_{14}H_{12}$, when the vapours of these bodies are passed through a red-hot tube; also, together with anthracene and other hydrocarbons, from toluene and xylene, by similar treatment (p. 428).

Phenanthrene is prepared from crude anthracene—the high-boiling portion of coal-tar—by collecting apart the portion which boils between 320° and 350°, and boiling the mass with alcohol. The solution on cooling deposits, first anthracene, and then phenanthrene, which may be obtained quite clear by two recrystallisations.

Phenanthrene crystallises in colourless shining laminæ, and exhibits a bluish fluorescence, especially in solution; melts at 100°; boils at 340°; dissolves in 50 parts of alcohol at 13°, easily in boiling alcohol, ether, and benzene. It unites with picric acid, a mixture of the saturated alcoholic solutions of the two bodies, depositing the compound $C_{14}H_{10}.C_0H_3(NO_2)_3O$, in reddish yellow needles melting at 143°. By boiling with chromic acid mixture phenanthrene is converted, first into phenanthrene-quinone and ultimately into diphenic acid (p. 572).

Phenanthrene tetrahydride, $C_{14}H_{14}$, formed by heating phenanthrene to 210°–240° with hydriodic acid and amorphous phosphorus, is a liquid boiling at 300°–310°.

Phenanthrene dibromide $C_{14}H_{16}Br_2$, obtained by direct combination in ethereal solution, forms prismatic crystals, and is resolved, by heating with water to 100°, into HBr and *bromophenanthrene*, $C_{14}H_9Br$, which melts at 63°.

Phenanthrene-quinone, $C_{14}H_8O_2$ = 

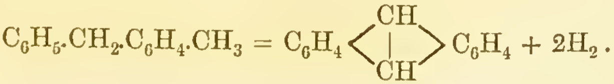
$$C_{14}H_8O_2 = \begin{array}{l} C_6H_4\text{—}CO \\ |\qquad\quad | \\ C_6H_4\text{—}CO \end{array}$$

, is formed by heating phenanthrene with chromic acid mixture, or by adding chromic anhydride to a solution of phenanthrene in glacial acetic acid. It crystallises from alcohol in shining orange-yellow needles, melts at 198°, sublimes without decomposition, dissolves sparingly in hot water and cold alcohol, easily in hot alcohol; dissolves in strong sulphuric acid with dark green colour, and is precipitated therefrom by water. It unites with acid sodium sulphite, forming the compound $C_{14}H_8O_2.SO_3NaH + 2H_2O$.

Phenanthrene-quinone is oxidised by chromic acid mixture to diphenic acid, and reduced by zinc-dust to phenanthrene; when ignited with soda-lime it yields diphenyl.

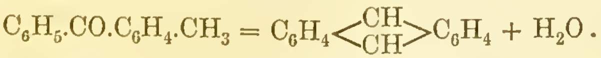
Phenanthrene-hydroquinone or *Dioxyphenanthrene*, $C_{14}H_8(OH)_2$, formed by the action of sulphurous acid on phenanthrene-quinone, crystallises in colourless needles, which, when exposed to the air, turn brown, and are reoxydised to the quinone. Its diacetyl-compound crystallises in tables melting at 202°.

Anthracene, $C_{14}H_{10}$.—This hydrocarbon may be formed artificially: 1. By passing benzyl-toluene through a red-hot tube or over heated lead oxide:



$$C_6H_5.CH_2.C_6H_4.CH_3 = C_6H_4\left\langle\begin{array}{c} CH \\ | \\ CH \end{array}\right\rangle C_6H_4 + 2H_2 .$$

2. By heating liquid phenyl-tolyl ketone (p. 571) with zinc-dust:



$$C_6H_5.CO.C_6H_4.CH_3 = C_6H_4{<}{\scriptstyle\begin{array}{c} CH \\ CH \end{array}}{>}C_6H_4 + H_2O .$$

3. Together with dibenzyl, by heating benzyl chloride with water to 190°:

$$4(C_6H_5.CH_2Cl) = C_{14}H_{16} + C_{14}H_{14} + 4HCl .$$

Anthracene is prepared from the high-boiling portions of coal-tar by repeated distillation, pressure, and recrystallisation from benzene. To obtain it quite pure and colourless, it must be sublimed at as low a temperature as possible—best by heating it till it begins to boil, and then blowing a strong current of air over it from a pair of bellows. Or its solution in hot benzene may be bleached by exposure to sunshine.

Anthracene crystallises in colourless monoclinic tables, exhibiting a fine blue fluorescence. It dissolves sparingly in alcohol and ether, easily in hot benzene; melts at 213°, and distils at a temperature a little above 360°. Its solution in benzene yields with picric acid the compound $C_{14}H_{10}.2C_6H_3(NO_2)_3O$, which crystallises in red needles.

A cold saturated solution of anthracene in benzene exposed to sunshine deposits tabular crystals of an isomeric modification, $C_{14}H_{10}$, called paranthracene. It is nearly insoluble in benzene, is not attacked by nitric acid or bromine, melts at 244°, and is at the same time converted into ordinary anthracene.

Anthracene dihydride, $C_{14}H_{12}$, formed by heating anthracene or anthraquinone with hydriodic acid and phosphorus, or by the action of sodium-amalgam on its alcoholic solution, crystallises in monoclinic tables easily soluble in alcohol, melting at 106°, distilling at 305°. On passing its vapour through a red-hot tube, it is resolved into anthracene and hydrogen. The *hexhydride*, $C_{14}H_{16}$, is formed by prolonged heating of anthracene or the dihydride with HI and phosphorus to 200°–220°, crystallises in laminæ, melts at 63°, boils at 290°. It is very soluble in alcohol, ether, and benzene, and is resolved at a red heat into anthracene and hydrogen.

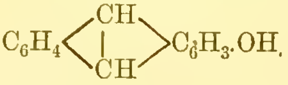
Anthracene dichloride, $C_{14}H_{10}Cl_2$, formed by passing chlorine gas over anthracene, crystallises in needles, and is converted by alcoholic potash into $C_{14}H_9Cl$. By heating anthracene in chlorine, dichloranthracene $C_{14}H_8Cl_2$ is formed, which crystallises in yellow laminæ, melts at 209°, and yields solutions having a splendid blue fluorescence.

Dibromanthracene, $C_{14}H_8Br_2$, is formed as the sole product of the action of bromine on a solution of anthracene on carbon sulphide. It crystallises in golden-yellow needles, melting at 221°, and is reconverted into anthracene by heating with alcoholic potash. *Dibromanthracene tetrabromide*, $C_{14}H_8Br_2.Br_4$, is formed by passing bromine vapour over finely divided anthracene or dibromanthracene. Hard, thick, colourless tables, melting with decomposition at 170°–180°.

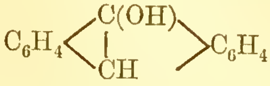
Another modification of dibromanthracene is formed by heating dibromanthraquinone with HI and phosphorus to 150° for eight hours. Golden-yellow tables, melting at 190°–192°, more soluble in alcohol and benzene than the preceding modification.

Anthracene-sulphonic acids, *mono-* and *di-*, are formed by heating anthracene with strong sulphuric acid, the former at 100°, the latter at 150°. The monosulphonic acid is produced in two isomeric modifications (α and β), which may be separated by means of their lead salts. That of the α acid (the chief product) crystallises in light yellow laminæ $(C_{14}H_9SO_3)_2Pb+4H_2O$, and is much more soluble than that of the β acid, which crystallises in prisms containing $7H_2O$.

Anthraphenols, $C_{14}H_{10}O = C_{14}H_9(OH)$.—Of these bodies there are two metameric modifications, viz.:



Anthrol.



Anthranol.

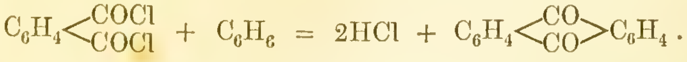
Anthrol is formed in two isomeric modifications by fusing the alkali-salts of the two isomeric anthracene-monosulphonic acids with potash or soda.

α. Light yellow needles or laminæ having a strong lustre, decomposing at 250° without previous fusing; insoluble in water, easily soluble in alcohol, ether, benzene, and alkalis. The alkaline solution absorbs oxygen from the air, and turns brown.

β. Yellowish prisms, somewhat less soluble in alcohol and ether than α, which it otherwise resembles in every respect.

Anthranol is formed by heating anthraquinone (20 parts) with hydriodic acid of 1·7 sp. gr. (80 parts) and phosphorus (4 parts) in a vessel with reversed condenser. It crystallises in yellowish needles, melts at 163°–170°, is nearly insoluble in cold, more soluble in hot alkalis. The solution absorbs oxygen from the air, and then deposits anthraquinone on boiling. Anthranol is also converted into anthaquinone by oxidation with nitric or chromic acid, and into anthracene by heating with zinc-dust. With acetic anhydride, it forms an acetic ether, $C_{14}H_9.O.C_2H_3O$, which crystallises in light yellow needles melting at 126°–131°.

Anthraquinone, $C_{14}H_8O_2 = C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_4$. — This compound, which may be regarded as a double ketone, and differs from the quinones of the benzene series in not having its two oxygen-atoms directly combined, is formed by oxidation of anthracene, anthracene-hydride, dichlor- or dibrom-anthracene, with nitric or chromic acid; also when liquid phenyl-tolyl ketone (p. 571), $C_6H_5.CO.C_6H_4.CH_3$, is passed over heated lead oxide, or heated with MnO_2 and sulphuric acid, or with chromic acid mixture; in small quantity also (together with benzophenone, p. 570) by distillation of calcium benzoate;—and by heating phthalic chloride and benzene with zinc-dust:



$$C_6H_4{<}{\substack{COCl\\COCl}} + C_6H_6 = 2HCl + C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_4 .$$

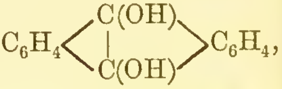
It is most easily prepared by adding finely pounded potassium dichromate, or a solution of chromic acid in glacial acetic acid, to a hot solution of anthracene in glacial acetic acid.

Anthraquinone sublimes in shining yellow needles, melts at 273°, dissolves in hot benzene and in nitric acid. It is a very stable compound, not easily altered by oxidising agents, and not reduced by sulphurous acid, like the quinones of the benzene series. Heated with hydriodic acid to 150°, or with zinc-dust, it is converted into anthracene. By fusion with potash at 250°, it yields 2 molecules of benzoic acid. Heated with PCl_5 to 190°–200°, it yields a mixture of di- and tetra-chloranthracene; and when heated with fuming sulphuric acid, it yields sulpho-acids, together with phthalic anhydride.

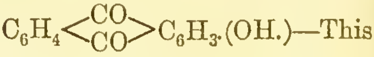
Dibromanthraquinone, $C_{14}H_6Br_2O_2$, is formed by heating anthraquinone with bromine to 100°, or by oxidising tetrabromanthracene with nitric acid; dichloranthraquinone is formed by a similar method. Both sublime in yellow needles, and are converted into alizarin by heating with potash-ley to 150°.

Dinitro-anthraquinone, $C_{14}H_8(NO_2)_2O_2$, obtained by boiling anthracene with dilute nitric acid, forms yellow needles melting at 280°, and, like picric acid, forms crystalline compounds with many hydrocarbons. An isomeric compound, obtained by the action of a mixture of nitric and sulphuric acids on anthraquinone, forms small light yellow monoclinic prisms, cakes together at 252°, and sublimes at a higher temperature in small needles, with partial decomposition.

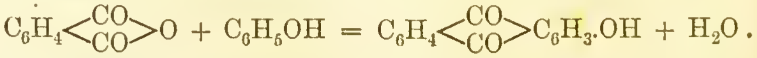
Anthraquinone-sulphonic acid, $C_{14}H_7O_2.SO_3H$, and the disulphonic acid, $C_{14}H_6O_2(SO_3H)_2$, are formed, together with phthalic anhydride, by heating anthraquinone with strong sulphuric acid to 250°–260°. The disulphonic acid is formed synthetically by heating orthobenzoyl-benzoic acid, $C_6H_5.CO.C_6H_4.CO_2H$ (p. 573), with fuming sulphuric acid. It forms yellow crystals easily soluble in water.



Anthrahydroquinone, $C_{14}H_8(OH)_2 = C_6H_4\left\langle\begin{array}{c}C(OH)\\ | \\ C(OH)\end{array}\right\rangle C_6H_4$, produced by heating anthraquinone with zinc-dust and potash-ley, forms yellow flakes, which, especially when moist, are quickly reconverted into anthraquinone by exposure to the air.



Oxyanthraquinone, $C_{14}H_8O_3 = C_6H_4\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle C_6H_3.(OH.)$—This compound is produced, together with alizarin, by fusing monobromanthraquinone or anthraquinone-sulphonic acid with potassium hydroxide; by boiling the product with water and calcium or barium carbonate, the alizarin is precipitated, and the oxyanthraquinone dissolved. Oxyanthraquinone is formed synthetically, together with its isomeride, *erythroxyanthraquinone*, by heating phthalic anhydride and phenol with strong sulphuric acid:



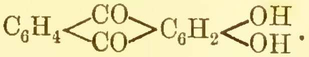
$$C_6H_4\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle O + C_6H_5OH = C_6H_4\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle C_6H_3.OH + H_2O\,.$$

The two isomerides may be separated by ammonia, in which oxyanthraquinone is soluble, erythroxyanthraquinone insoluble.

Oxyanthraquinone is equally soluble in hot and in cold alcohol, crystallises in sulphur-yellow needles, melts at 268°–271°, and sublimes with some difficulty in laminæ. It dissolves readily in ammonia, baryta-water and lime-water, and decomposes barium carbonate when boiled with it in water.

Erythroxyanthraquinone is more soluble in hot than in cold alcohol, crystallises in orange-yellow needles, melts at 173°–180°, and sublimes at 150°. It is nearly insoluble in dilute ammonia, forms dark red lakes with baryta- and lime-water, and (like alizarin) does not decompose carbonate of barium. Both oxyanthraquinones are converted by fusion with potash into alizarin.

Dioxyanthraquinones, $C_{14}H_8O_4 = C_{14}H_6(OH)_2O_2$.—This formula includes eight known compounds, in three of which the two hydroxyl-groups are situated in the same benzene-nucleus, while four others have one hydroxyl in each benzene-nucleus, and in the eighth, the position of these groups is uncertain.

I. *Dioxyanthraquinones*, 
$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{OH\\OH}$.

1. ALIZARIN.—This compound, in which the two hydroxyls are supposed to stand to one another in the para-position, is the red colouring matter of madder root (*Rubia tinctorum*). Fresh madder roots contain a glucoside, called ruberythric acid, which, when the roots are steeped in water, is resolved, under the influence of a peculiar ferment also contained in them, into alizarin and glucose :

$$\underset{\text{Ruberythric acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

In old roots this change has already taken place to a considerable extent, so that they contain free alizarin. This spontaneous change was the basis of the older method of obtaining alizarin, and of the use of madder in dyeing. Various methods of accelerating the decomposition have been invented, in particular the treatment of the pulverised root, previously exhausted with water, with strong sulphuric acid, which decomposes the ruberythric acid in the manner above explained, but does not alter the resulting alizarin. The product thus obtained is called garancin.

At present, however, almost all the alizarin used in dyeing is obtained by artificial processes from anthracene. It may be obtained by the action of melting potash on various derivatives of anthracene, viz., dibrom- and dichlor-anthraquinone, the two monoxyanthraquinones, and anthraquinone-disulphonic acid. Graebe and Liebermann, in 1868, first prepared it from dibromanthraquinone, and Perkin soon afterwards showed that it might be obtained much more economically from anthraquinone-disulphonic acid. This last method is now carried out on a very large scale. The mass obtained by fusion with potash is dissolved in water, and the alizarin, precipititated by hydrochloric acid, is purified by crystallisation and sublimation.

Alizarin crystallises from alcohol in reddish-yellow prisms or needles containing 3 mol. H_2O, which it gives off at 100°. It melts at 275° (Liebermann a. Troschke); at 289°–290° (Claus a. Willgerodt),* and sublimes in orange-coloured needles; dissolves sparingly in hot water, easily in alcohol and ether; also in strong sulphuric acid, forming a dark red solution, from which it is precipitated by water in its original state.

Alizarin has the structure of a diatomic phenol, and reacts like a weak acid. It dissolves in alkalis, forming purple solutions, from which calcium and barium salts throw down the corresponding salts as purple precipitates (distinction from monoxyanthraquinone).

Aluminium- and tin-salts form red precipitates (madder-lakes); ferric salts, a black-violet precipitate. The use of alizarin in dyeing and calico-printing is founded on this property of forming insoluble coloured compounds with metallic salts.

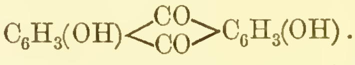
Alizarin is converted by heating with zinc-dust into anthracene, and by oxidation with nitric acid into phthalic acid.

Alizarin boiled with acetic anhydride yields first *monacetyl-alizarin,* $C_{14}H_6(OH)(OC_2H_3O)O_2$, and after prolonged boiling, *diacetyl-alizarin,* $C_{14}H_6(OC_2H_3O)_2O_2$.

Alizarinamide, $C_6H_4.C_2O_2.C_6H_2(NH_2)OH$, formed by heating alizarin with aqueous ammonia to 150°–200°, crystallises in brown needles, melting at 250°–260°.

2. Quinizarin is formed by heating phthalic anhydride and hydroquinone, or parachlorophenol, with sulphuric acid. It crystallises from ether in yellow needles melting at 194°; dissolves in alkalis with blue-violet colour; forms blue-violet precipitates with baryta and magnesia, red with alumina; and is reduced to anthracene by heating with zinc-dust.

3. Purpuroxanthin (or *Xanthopurpurin*) occurs in small quantity in madder, and is formed from purpurin by reduction with stannous chloride in alkaline solution. Yellowish red needles, m. p. 262°–263°; dissolving with red colour in alkalis and baryta-water. In alkaline solution it absorbs oxygen from the air.



II. *Dioxyanthraquinones,* $C_6H_3(OH){<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_3(OH)$.

4. Anthraflavone. — Formed from oxybenzoic acid, $C_6H_4(OH).CO.OH$, in small quantity by dry distillation, in larger quantity by heating with sulphuric acid to 180°-200°. Crystallises in small yellow needles; sublimes above 300° with partial decomposition, and without previous fusion; nearly insoluble in boiling water, slightly soluble in ether, more easily in alcohol; dissolves with brown colour in alkalis; converted into alizarin by heating with zinc-dust; into oxybenzoic acid by fusion with potash.

5. Anthraflavic Acid.—Formed, together with isoanthraflavic acid, from two different anthraquinone-disulphonic acids, in the preparation of alizarin on the large scale. It is therefore a constituent of crude commercial alizarin, and may be extracted therefrom

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* Deutsch. Ch. Ges. Ber. 1875, pp. 351, 381.

by lime-water (the alizarin remaining undissolved), the red solution being precipitated with hydrochloric acid, and the precipitate treated with cold baryta-water, which dissolves iso-anthraflavic acid, and leaves the anthraflavic acid undissolved.

Anthraflavic acid crystallises from alcohol in anhydrous yellow silky needles; melts above 330°; dissolves in alkalis, with yellowish red colour; forms with acetic anhydride a *diacetyl-compound*, $C_{14}H_6(OC_2H_3O)_2O_2$, melting at 227°.

6. ISO-ANTHRAFLAVIC acid, prepared as above, crystallises from aqueous alcohol in long yellow needles with 1 mol. H_2O, which is given off at 150°; the anhydrous compound melts above 330°. Dissolves in alkalis with deep red colour. The diacetyl-compound forms small pale-yellow crystals melting at 195°.

7. CHRYSAZIN, prepared by heating with alcohol the diazo-compound formed by the action of nitrous acid on sulphate of hydrochrysammide (*infra*), crystallises in golden-yellow laminæ or red-brown highly lustrous needles; melts at 191°; dissolves in alkalis with yellowish red colour; forms insoluble red compounds with lime- and baryta-water; is reduced to anthracene by heating with zinc-dust. The diacetyl-compound forms yellowish laminæ melting at 226–230°.

Tetranitrochrysazin or *Chrysammic acid*, $C_{14}H_2(NO_2)_4(OH)_2O_2$, formed by heating aloes, or chrysazin, with strong nitric acid, crystallises in golden yellow laminæ sparingly soluble in water, and reacts like a strong bibasic acid. By the action of reducing agents it is converted into tetramido-chrysazin or chrysammide, $C_{14}H_2(NH_2)_4(OH)_2O_2$, which crystallises in indigo-blue needles, having a splendid coppery lustre.

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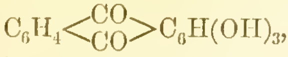
8. FRANGULIC ACID, $C_{14}H_8O_4 + 1\frac{1}{2}H_2O$, a dioxyanthraquinone in which the relative positions of the two OH-groups are not known, is formed by the action of dilute acids on frangulin $C_{20}H_{20}O_{10}$, a glucoside contained in the bark of *Rhamnus frangula*. It crystallises in orange-yellow needles or plates containing $1\frac{1}{2}$ mol. H_2O, gives off its water at 180°, and melts at 252°–254°. Reduced by zinc-dust to anthracene.

Trioxyanthraquinones, $C_{14}H_8O_5 = C_{14}H_5(OH)_3O_2$. — Of these compounds there are four known modifications:

1. PURPURIN,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H(OH)_3$, occurs in old madder-root, together with alizarin, and may be separated by means of boiling alum solution, in which the alizarin is insoluble. It may be formed artificially from alizarin or chrysazin by oxidation with MnO_2 and sulphuric acid at 140°–160°, and from purpuroxanthin by merely heating the alkaline solution in an open vessel. It crystallises in reddish-yellow prisms, easily fusible, and subliming with partial decomposition; somewhat more soluble in

water than alazarin; dissolves with red colour in alcohol, ether, and alkalis; forms purple-red precipitates with lime- and baryta-water; is reduced to anthracene by heating with zinc-dust. With acetic anhydride it forms a *triacetyl-compound*, $C_{14}H_5(OC_2H_3O)_3O_2$, which crystallises in yellowish needles melting at 190°–193°.

Purpurinamide, $C_{14}H_5(NH_2)(OH)_2O_2$, obtained by heating purpurin with aqueous ammonia, forms brownish-green metallically lustrous needles. Treated in hot alcoholic solution with nitrous acid, it is converted into purpuroxanthin.

2. ANTHRAPURPURIN, $C_6H_3OH.C_2O_2.C_6H_2(OH)_2$, produced by fusing potassium anthraquinone-disulphonate or isanthraflavic acid with potash, forms orange-coloured needles, melting above 330°, sublimable with partial decomposition. Dissolves in alkalis with fine violet colour, and, like alizarin, produces red colours with alumina-mordants, purple and black with iron mordants; but the reds are purer than those of alizarin, the purples bluer, and the blacks more intense. Its triacetyl-compound forms light yellow scales melting at 220°–222°.

3. FLAVOPURPURIN, $C_6H_3OH.C_2O_2.C_6H_2(OH_2)$, formed from anthraflavic acid by fusion with potash, crystallises from alcohol in golden-yellow needles, melts above 330°, sublimes in long needles, like alizarin. Dissolves easily in alcohol, with purple colour in alkalis.

4. OXYCHRYSAZIN, $C_6H_3(OH).C_2O_2.C_6H_2(OH)_2$, produced by the action of melting potash on chrysazin, is precipitated from its bluish violet solution in alkalis by acids in brown flocks, and crystallises from alcohol. Its triacetyl-compound forms light yellow needles melting at 192°–193°.

Tetraoxyanthraquinone, $C_{14}H_4(OH)_4O_2$, is known in two modifications:

1. ANTHRACHRYSONE, $C_6H_2(OH)_2.C_2O_2.C_6H_2(OH)_2$, is formed, like anthraflavone, from dioxybenzoic acid, $C_6H_3(OH)_2.CO.OH$, by dry distillation, or by heating to 140° with strong sulphuric acid. It is insoluble in water, crystallises from glacial acetic acid or from alcohol in yellowish red needles, melting at 320°; yields anthracene when heated with zinc-dust.

2. RUFIOPIN, $C_{14}H_4(OH)_4O_2$, obtained by heating opianic acid (p. 550) with sulphuric acid, forms yellowish red needles or crusts, dissolving in alkalis with violet-red colour; yields anthracene by reduction with zinc-dust.

A third modification is perhaps *Pseudopurpurin*, which is contained in madder-root. It is very much like purpurin, is converted into that substance by boiling with water or alcohol, and is said to be converted by reducing agents into purpuroxanthin.

Rufigallic acid, $C_{14}H_8O_8$, obtained by heating gallic or digallic acid with strong sulphuric acid, is a hexoxyanthraquinone, $C_6H(OH)_3.C_2O_2.C_6H(OH)_3$. It forms small, shining, brown-red crystals, containing $2H_2O$, which it gives off at 120°, and sublimes at a higher temperature in cinnabar-red prisms; dissolves sparingly in hot water, alcohol, and ether, with brown colour in alkalis; precipitated with indigo-blue colour by baryta-water. Yields anthracene by reduction with zinc-dust.

Methyl-anthracene, $C_{15}H_{12} = C_{14}H_9.CH_3$, is formed by passing the vapour of ditolyl-methane or ditolyl-ethane (p. 565) through a red-hot tube, and by heating chrysophanic acid, emodin or aloïn, with zinc-dust. Colourless shining laminæ, melting at 200°; slightly soluble in alcohol, ether, and glacial acetic acid; easily in chloroform, CS_2, and benzene. Forms with *picric acid* a compound which crystallises in long dark-red needles, and is decomposed by water and alcohol.

Methylanthraquinone, $C_{15}H_{10}O_2 = C_6H_4.C_2O_2.C_6H_3(CH_3)$, obtained by oxidising methylanthracene in alcoholic solution with nitric acid, forms small yellow needles melting at 162°–163°.

Dioxymethylanthraquinone, $C_{15}H_{10}O_4 = C_{14}H_5.CH_3(OH)_2.O_2$, is known in two modifications:

1. Methylalizarin is formed by the action of melting potash on the potassium salt of methylanthraquinone-sulphonic acid. It closely resembles alizarin; sublimes above 200° in tufts of small red crystals; melts at 250°–252°; dissolves in alkalis with blue-violet colour.

2. Chrysophanic acid (*Parietic acid, Rheic acid*), occurs in the lichen *Parmelia parietina*, in senna leaves, and in rhubarb root, and may be extracted therefrom by ether or alkalis. It crystallises in golden-yellow needles or prisms, melts at 162°, and sublimes partly without decomposition; dissolves in alkalis with red colour; is reduced by zinc-dust to methyl-anthracene.

Trioxymethylanthraquinone or *Emodin,* $C_{15}H_{10}O_5 = C_{14}H_4(CH_3)(OH)_3.O_2$, occurs in the bark of *Rhamnus frangula*, and in small quantity, together with chrysophanic acid, in rhubarb root, and is separated by solution of sodium carbonate, which dissolves the emodin, leaving the chrysophanic acid. Long, brittle orange-red, monoclinic prisms, melting at 245°–250°; converted into methyl-anthracene by heating with zinc-dust.

Anthracene-carbonic Acid, $C_{14}H_9.CO_2H$, is obtained by heating anthracene with carbonyl chloride to 200° in sealed tubes, dissolving the product in sodium carbonate, and precipitating with hydrochloric acid. Long, silky, light yellow needles, melting with decomposition at 206°; slightly soluble in hot water, easily in alcohol. Oxidised by chromic acid to anthraquinone; resolved by heat into CO_2 and anthracene. An isomeric acid, obtained by saponification of the cyanide produced by heating potassium anthracenesulphonate with potassium ferrocyanide, melts above 220°, and sublimes without decomposition in orange-yellow needles.

Hydrocarbons of Higher Boiling Point.

Pyrene, $C_{16}H_{10}$, and **Chrysene**, $C_{18}H_{12}$, are contained in the portion of coal-tar boiling above 360° (b. p. of anthracene), and may be separated by heating the solid mass with carbon sulphide, which dissolves pyrene, together with other hydrocarbons, while the chrysene remains behind.

Pyrene may be obtained pure by distilling off the carbon sulphide, dissolving the residue in alcohol, and adding an alcoholic solution of picric acid. Red crystals then separate, consisting of a compound of pyrene and picric acid, which, after purification by repeated crystallisation from alcohol, may be decomposed by ammonia. Pyrene crystallises in plates, melts at 142°, and distils at a higher temperature; dissolves sparingly in cold, more readily in hot alcohol; very easily in benzene, ether, and carbon sulphide. Its picric acid compound, $C_{16}H_{10}.C_6H_3(NO_2)_3O$, crystallises in red needles. Heated with hydriodic acid to 200°, it is converted into a hexhydride, $C_{16}H_{10}.H_6$, melting at 127°. Heated with chromic acid mixture, it yields pyrene-quinone, $C_{16}H_8O_2$, which sublimes in red needles.

Chrysene, $C_{18}H_{12}$, the portion of the high-boiling coal-tar hydrocarbons which is insoluble in carbon sulphide, may be purified by repeated crystallisation from benzene. It is thus obtained in bright yellow glistening scales, which cannot be decolorised by recrystallisation, but may be obtained quite colourless by heating with hydriodic acid and amorphous phosphorus to 240°, or by boiling with alcohol and a small quantity of nitric acid. It dissolves very sparingly in alcohol, ether, and carbon sulphide, more freely in benzene; sublimes in dazzling white laminæ, which exhibit a fine blue fluorescence, and melt at 250°. Its picric acid compound $C_{18}H_{12}.C_6H_3(NO_2)_3O$ crystallises in brown needles. By oxidation with chromic anhydride dissolved in glacial acetic acid, it yields chrysene-quinone, $C_{18}H_{10}O_2$, which crystallises in red needles, melts at 235°, dissolves with fine blue colour in strong sulphuric acid, and is precipitated from the solution by water in its original state. Chrysene-quinone unites with acid sodium sulphite, and is reduced by sulphurous acid to chrysohydroquinone, $C_{18}H_{10}(OH)_2$. By distillation with soda-lime it yields the hydrocarbon $C_{16}H_{12}$ (m. p. 104°–105°), just as phenanthrene-quinone yields diphenyl (p 561).

Retene, $C_{18}H_{18}$, occurs in thin unctuous scales on fossil pine-stems, in beds of peat and lignite, in Denmark and other localities. It is produced in the dry distillation of very resinous fir and pine-wood, passing over together with the heavy tar-oil, and separating in scales like paraffin; also, together with other hydrocarbons, by passing acetylene through red-hot tubes. It crystallises in colourless laminæ, slightly soluble in alcohol, easily in ether; melts at 99°; forms with picric acid the compound $C_{18}H_{18}.C_6H_3(NO_2)_3O$, which crystallises in orange-yellow needles; is converted by sulphuric acid into a disulphonic acid, and by chromic acid mixture into dioxyretistene, $C_{16}H_{14}O_2$ (m. p. 194°–195°) and phthalic acid. Dioxyretistene, heated with zinc-dust, is converted into retistene, $C_{16}H_{14}$, which crystallises from alcohol in white laminæ, and forms a crystalline compound with picric acid.

Similar but less known hydrocarbons are *Fichtelite*, found on old pine-stems ; *Idrialin*, in quicksilver ore from Idria ; and *Scheererite*, in beds of lignite.

TERPENES and CAMPHORS.

The terpenes, $C_{10}H_{16}$, are volatile oils existing in plants, chiefly of the coniferous and aurantiaceous orders. They have not yet been formed by any artificial process, but their relation to the aromatic group is shown by their conversion into terephthalic acid by oxidation with nitric acid, and by the formation of cymene from turpentine oil (p. 431).

Turpentine oil, the most important member of the group, is contained in the wood, bark, leaves, and other parts of pines, firs, and other coniferous trees, and is usually prepared by distilling crude turpentine, the oleo-resinous juice which exudes from incisions in the bark of the trees, either alone or with water. It was formerly supposed that all the volatile oils thus obtained, and having the composition $C_{10}H_{16}$, were identical in chemical and physical properties; but recent investigations, especially those of Berthelot, have shown that the turpentine oils obtained from different sources exhibit considerable diversities in their physical, and more especially in their optical properties; further, that most kinds of turpentine oil are mixtures of two or more isomeric or polymeric hydrocarbons, differing in physical and sometimes also in chemical properties. These modifications are often produced by the action of heat and of chemical reagents during the purification of the oil.

The several varieties of turpentine oil, when purified by repeated rectification with water, are colourless mobile liquids, having a peculiar aromatic but disagreeable odour. They are insoluble in water, slightly soluble in aqueous alcohol, miscible in all proportions with absolute alcohol, ether, and carbon disulphide. They dissolve iodine, sulphur, phosphorus, and many organic substances which are insoluble in water, such as fixed oils and resins, and are therefore used for making varnishes.

The principal varieties are, French turpentine oil, obtained from the French or Bordeaux turpentine of *Pinus maritima,* and English turpentine oil, from the turpentine collected, in Carolina and other Southern States of the American Union, from *Pinus australis* and *Pinus Tæda.*

French turpentine oil, when purified by neutralising it with an alkaline carbonate, and then distilling it, first over the water-bath, and then in a vacuum (by which treatment all transformation of the product by heat or by reagents is avoided), consists mainly of a hydrocarbon, $C_{10}H_{16}$, called terebenthene. It has a specific gravity of 0·864, boils at 161°, and turns the plane of polarisation of a ray of light to the left. English turpentine oil, treated in a similar manner, yields, as its chief constituent, a liquid called australene, or austraterebenthene, having the same specific gravity and boiling point as terebenthene, but turning the plane of polarisation to the right.

When pure turpentine oil (terebenthene or australene) is heated to 200°–250°, it undergoes a molecular transformation, and may then be separated by distillation into two oils, one called austrapyrolene, isomeric with the original oil, and boiling at 176°–178°; the other, called metaterebenthene, polymeric with the original oil, having the formula $C_{20}H_{32}$, and boiling at a temperature above 360°. Both are levorotatory, the latter exhibiting the greater amount of rotatory power.

Turpentine oil is converted, by repeated distillation with a small quantity of strong sulphuric acid, into two inactive modifications, terebene, $C_{10}H_{16}$, boiling at 160°, and colophene, $C_{20}H_{32}$, boiling at a very high temperature. A body of the same percentage composition, and closely resembling terebene in its physical properties, is obtained by the action of bromine and alcoholic potash on diamylene (p. 58): $C_{10}H_{20} - H_4 = C_{10}H_{16}$.

Turpentine oil exposed to the air absorbs oxygen, and acquires powerful oxidising properties, formerly supposed to be due to the conversion of the oxygen into ozone; but according to recent experiments by Kingzett,* it appears highly probable that the oxidising compound is an organic peroxide, $C_{10}H_{14}O_4$, which when heated with water is resolved into hydrogen dioxide and camphoric acid: $C_{10}H_{14}O_4 + 2H_2O = H_2O_2 + C_{10}H_{16}O_4$.

Nitric acid and other powerful oxidising agents, convert turpentine oil into a number of acid products of complex constitution. Strong nitric acid acts very violently on turpentine oil, sometimes setting it on fire.

Chlorine is absorbed by turpentine oil, with evolution of heat, sometimes sufficient to produce inflammation. When paper soaked in rectified turpentine oil is introduced into a vessel filled with chlorine, the turpentine takes fire, and a quantity of black smoke is produced, together with white fumes of hydrochloric acid. *Bromine* acts in a similar manner. *Iodine* is dissolved by turpentine oil, forming at first a green solution, which afterwards becomes hot, and gives off hydriodic acid. When a considerable quantity of iodine is suddenly brought in contact with turpentine oil, explosion frequently ensues. Turpentine oil distilled with *chloride of lime* and *water*, yields chloroform.

Nitrosoterpene, $C_{10}H_{15}(NO)$.—When gaseous nitrosyl chloride, NOCl (obtained by passing the gases evolved from heated nitrohydrochloric acid into strong sulphuric acid, and heating the resulting solution with sodium chloride), is passed into oil of turpentine cooled by ice and salt, a white crystalline substance is precipitated, having the composition $C_{10}H_{10}.NOCl$, and this when heated with alcoholic soda gives up HCl, and is converted into nitrosoterpene. On acidulating with acetic acid, evaporating to dryness, washing the residue with water, and crystallising it from alcohol, the nitrosoterpene is obtained in monoclinic crystals melting at 129°–130°, and subliming at a somewhat higher temperature. It burns easily, but is not explosive. Sodium-amalgam reduces it to a hydrocarbon.

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* Chem. Soc. Jour. 1874, 511; 1875, 214.

Compounds of Turpentine oil.—Turpentine oil forms several compounds with *hydrochloric acid.* The gaseous acid converts it into the monohydrochloride, $C_{10}H_{16}.HCl$. On the other hand, when the oil is subjected for several weeks to the action of the strong aqueous acid, crystals of a dihydrochloride, $C_{10}H_{16}.2HCl$, are obtained. This latter compound is also formed by the action of hydrochloric acid gas on *lemon oil:* hence it is called citrene dihydrochloride. By the action of hydrochloric acid on terebene, the compound $C_{20}H_{32}.HCl$ is formed, called diterebene hydrochloride. Lastly, when a current of hydrochloric acid gas is passed through a solution of turpentine oil in acetic acid, the compound $C_{20}H_{32}.3HCl$ is produced, called dipyrolene hydrochloride.

Hydrobromic and *hydriodic acids* form, with oil of turpentine, compounds analogous in composition to the hydrochlorides; the dihydriodide, however, has not been obtained from turpentine oil itself.

Whatever method may be adopted for preparing the hydrochlorides, hydrobromides, or the monohydriodide of turpentine oil, there are always two isomeric modifications obtained—one liquid, the other solid and crystalline. The crystallised monohydrochloride is sometimes, though inappropriately, designed as *artificial camphor*, and the dihydrochloride as *lemon camphor.*

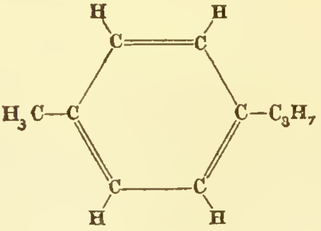
Hydrates.—Turpentine oil left in contact with water generally changes into a crystalline compound $C_{10}H_{10}.3H_2O$ called terpin hydrate, which is more easily obtained by leaving a mixture of 8 pts. turpentine oil, 2 pts. nitric acid of specific gravity 1·25, and 1 pt. alcohol exposed to the air in a shallow vessel. It forms rhombic crystals, inodorous, easily soluble in water, alcohol, and ether. It melts below 100°, giving off water, and being converted into a white crystalline mass called terpin, having the composition $C_{10}H_{10}.2H_2O$, or $C_{10}H_{18}(OH)_2$, which melts at 103°, and sublimes in slender needles; with bromine at 50° it forms a bromide which, when distilled, yields cymene.

By heating the aqueous solution of terpin with a small quantity of hydrochloric acid, or by boiling the dihydrochloride, $C_{10}H_{16}.2HCl$, with water or alcoholic potash, terpinol, $2C_{10}H_{16}.H_2O$, is obtained as an oil, smelling like hyacinths, and distilling at 168°.

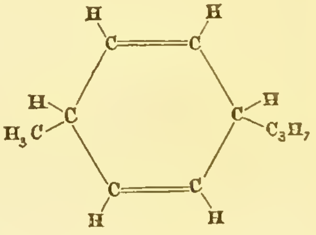
Constitution and Combining Capacity of Turpentine Oil.—The hydrocarbon $C_{10}H_{16}$ acts as a quadrivalent radicle, capable of uniting with four monad atoms, and therefore with two molecules of the acids HCl, HBr, and HI, thereby producing the dihydrochlorides, &c., above mentioned; but, like other tetrad radicles, it can also take up only two monad atoms, producing the monohydrochloride, &c. The same tetrad radicle, by doubling itself, loses two units of equivalence,—just as two atoms of carbon when united are satisfied by six, and not by eight atoms of hydrogen,—and forms the hydrocarbon, $C_{20}H_{32}$, which is sexvalent, and can therefore form such compounds as $C_{20}H_{32}.3HCl$. Further, this same hexad radicle might form non-saturated compounds containing only four or two monad atoms; in reality, however, only those containing two monad atoms are known, such as $C_{20}H_{32}.HCl$.

If in the several hydrochlorides each atom of chlorine be replaced by hydroxyl, HO, we obtain the formulæ of the several hydrates of turpentine oil; the hydrate corresponding with the hydrochloride $C_{20}H_{32}.3HCl$, has not, however, been prepared.

The formation of cymene from turpentine, by first converting the latter into the dibromide $C_{10}H_{16}Br_2$, and then abstracting H_2Br_2 (p. 431), shows that turpentine oil is a hydride of cymene. Now cymene is methyl-propyl-benzene, $C_6H_4.(CH_3)(C_3H_7)$: hence the relation of the two hydrocarbons may be represented by the following formulæ:—



Cymene.



Turpentine oil.

The presence of two lateral chains in the molecule in the position 1:4, is in accordance with the formation of terephthalic acid by oxidation of turpentine oil. The other products of its oxidation are likewise in accordance with this view of the constitution of turpentine oil. Other arrangements of the radicles CH_3 and C_3H_7 in the molecule are, however, conceivable, and may perhaps give rise to some of the isomeric modifications of turpentine oil and its congeners. Other modifications may arise from the hydration of other metameric forms of the molecule $C_{10}H_{14}$, *e.g.*, ethyldimethyl-benzene and tetramethyl-benzene.

The formula of turpentine oil above given, in which the double union of one pair of carbon-atoms in cymene is loosened, represents the molecule as saturated. A similar loosening of a second pair would render the molecule bivalent, and therefore capable of taking up 1 mol. of HCl, HBr, Br_2, &c., and the loosening of the third pair would render it quadrivalent and capable of uniting with 2HCl, 2HBr, &c.

Acids produced by Oxidation of Turpentine-Oil.—Turpentine-oil boiled with dilute nitric acid yields formic, acetic, butyric, oxalic, terebic, toluic, and terephthalic acids.

Terebic acid, $C_7H_{10}O_4$, crystallises in shining prisms, easily soluble in hot water and alcohol; melts at 175°, and sublimes at a lower temperature. By distillation it is resolved into CO_2, and pyroterebic acid $C_6H_{10}O_2$ (p. 309). By boiling with carbonates it forms salts, $C_7H_9M'O_4$, which by the action of strong bases are converted into salts $C_7H_{10}M'_2O_5$, called diaterebates, the acid of which, $C_7H_{12}O_5$, cannot be obtained in the free state, as when separated from the salts, it is immediately resolved into water and terebic acid.

Terpin heated to 400° with soda-lime is converted into terebentilic acid, $C_8H_{10}O_2$, which crystallises from hot water and alcohol in slender needles melting at 90°, and distilling at 250°. By oxidation with chromic acid mixture, terpin yields terpenylic acid, $C_8H_{13}O_4$, which is monobasic, crystallises from water with 1 mol. H_2O, and melts in the dehydrated state at 90°.

Volatile or Essential Oils.—The volatile oils obtained from plants by pressure, or by distillation with water, consist either of hydrocarbons, isomeric or polymeric with turpentine oil, or of mixtures of these hydrocarbons with compounds of carbon, hydrogen, and oxygen. Those obtained from aurantiaceous plants are terpenes distinguished by their fragrant odour. Lemon oil, from the rind of the fruit of *Citrus Limonum*, consists mainly of citrene, $C_{10}H_{16}$, a dextrorotatory terpene, closely resembling terebenthene, having a specific gravity of 0·85 at 15°, boiling at 167° or 168°. With water it forms a crystallised hydrate resembling terpin; with hydrochloric acid, a dihydrochloride, $C_{10}H_{16}.2HCl$, existing in a solid and liquid modification, and a monohydrochloride, $C_{16}H_{16}.HCl$, apparently susceptible of similar modifications.

Similar oils are obtained from the rind of the sweet orange (*Citrus aurantium*), the bergamot (*C. bergamia*), the bigarade or bitter orange (*C. bigaradia*), the lime (*C. Limetta*), the sweet lemon (*C. lumia*), and the citron (*C. medica*). Oil of neroli, obtained by distilling orange flowers with water, is probably also a terpene when pure.

The volatile oils of athamanta, beech, borneo (from *Dryabalanops Camphora*), caoutchouc, caraway, camomile, coriander, elemi, gomart, hop, juniper, imperatoria, laurel, parsley, pepper, savin, thyme, valerian, and others, also the neutral oils of wintergreen (*Gaultheria procumbens*), and cloves, are isomeric with oil of turpentine. The oils of copaiba and cubebs are probably polymeric with it, their molecules containing $C_{20}H_{32}$.

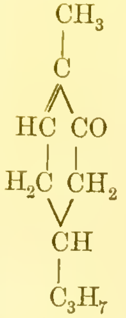
As examples of volatile oils containing an oxygenised constituent mixed with a terpene, may be mentioned valerian oil, which contains valeric acid, $C_5H_{10}O_2$; pelargonium oil containing pelargonic acid, $C_9H_{18}O_2$; rue oil, containing euodic aldehyde, $C_{11}H_{22}O$; wintergreen oil, containing acid methyl salicylate, $C_8H_8O_3$. Some volatile oils consist essentially of aldehydes: thus bitter almond oil consists of benzoic aldehyde, C_7H_6O; the oils of cinnamon and cassia contain cinnamic aldehyde, C_7H_8O; and those of anise, star-anise, fennel, and tarragon, contain anethol, $C_{10}H_{12}O$. Those volatile oils which exist ready formed in living plants do not appear to contain any elements besides carbon, hydrogen, and oxygen. Sulphur is found only in certain oils resulting from a kind of fermentation process, as in the volatile oils of mustard and garlic; nitrogen, when it occurs, must be regarded as an impurity resulting from admixed vegetable tissue.

A few volatile oils are found in the bodies of animals,—oil of ants, for example.

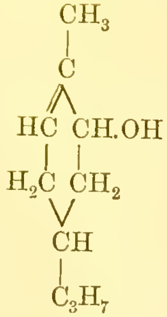
Most volatile oils are colourless when pure; they often, however, have a yellow colour arising from impurity; and a few, the oils of wormwood and camomile, for example, have a green or blue colour, due to the presence of an oily compound of a very deep blue colour, called *cerulein.* They have usually a powerful odour, and a pungent burning taste. When exposed to the air they frequently become altered by slow absorption of oxygen, and assume the character of resins. They mix in all proportions with fat oils, such as linseed, nut, colza, and whale oils, and dissolve freely both in ether and alcohol: from the latter solvent they are precipitated by the addition of water. Volatile oils communicate a greasy stain to paper, which disappears by warming; by this character any adulteration with fixed oils can be at once detected. Many volatile oils, when exposed to cold, separate into a solid crystalline compound called a *stearoptene*, and a liquid oil, which, for distinction, is sometimes called an *elæoptene.*

Camphors.

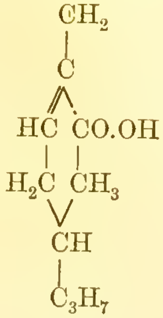
These are oxygenated crystalline compounds, having a peculiar odour. They contain 10 atoms of carbon, and are nearly related to the terpenes, with which they are associated in plants, and by the oxidation of which they appear to be formed. The principal members of the group are common camphor, $C_{10}H_{16}O$, and borneo-camphor or borneol, $C_{10}H_{18}O$, which stand to one another in the relation of a ketone to a secondary alcohol. The constitution of these bodies is not completely established, but their intimate relation to cymene, $C_{10}H_{14}$ (p. 433), and carvacrol, $C_{10}H_{14}O$ (p. 489), **cymene** being produced by heating common camphor with zinc chloride or phosphorus pentasulphide, and carvacrol by heating the same substance with iodine, render it probable that they and their nearest products of oxidation may be represented by the following formula:—



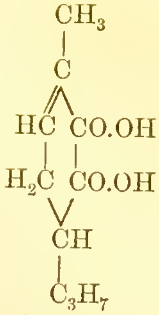
Common Camphor.



Borneol.



Campholic acid.



Camphoric acid.

Common Camphor, Laurel Camphor, or **Japan Camphor,** $C_{10}H_{16}O$, occurs in all parts of the camphor-tree of China and Japan (*Laurus Camphora*), often deposited in distinct crystals; it is obtained by distilling the woody parts with water, and purified by sublimation. It has been produced artificially in small quantity by oxidation of oil of sage and oil of valerian (*i.e.*, of the terpenes contained in them) by nitric acid; of turpentine oil by potassium permanganate; of camphene (from borneol) by platinum-black or chromic acid mixture; also by oxidation of cymene.

Common camphor is a colourless translucent mass, tough and difficult to powder, having a strong and peculiar taste and smell, and a density of 0·985. Small pieces thrown on water move about with a rotatory motion. It volatilises at ordinary temperatures, melts at 175°, and distils at 204°. It dissolves sparingly in water, easily in alcohol, ether, acetic acid and volatile oils; and crystallises from alcohol—also by sublimation—in shining strongly refractive crystasl. The alcoholic solution is dextro-rotatory: $[\alpha] = +47{\cdot}4°$.

By distillation over fused zinc chloride, or with phosphoric anhydride, camphor is resolved into water and cymene: $C_{10}H_{16}O = C_{10}H_{14} + H_2O$, considerable quantities of mesitylene, toluene, xylene, and other hydrocarbons being, however, formed at the same time. The formation of cymene takes place more definitely when camphor is distilled with phosphorus pentasulphide, thiocymene, $C_{10}H_{13}SH$ being formed at the same time. Heated with iodine ($\frac{1}{2}$ part) it yields carvacrol. By heating with alcoholic potash it is resolved into borneol and camphic acid, just as benzaldehyde is resolved into benzyl alcohol and benzoic acid:

$$2C_{10}H_{16}O + KOH = C_{10}H_{18}O + C_{10}H_{15}KO_2.$$

By heating with nitric acid, camphor is converted into camphoric and camphoronic acids; heated to 400° with soda-lime, it yields campholic acid, $C_{10}H_{18}O_2$.

Camphor, heated with *bromine* to 110°–120°, yields crystalline $C_{10}H_{15}BrO$ (m. p. 75°; b. p. 275°), and $C_{10}H_{14}Br_2O$ (m. p. 214°,

b. p., 285°). Camphor dissolved in chloroform takes up bromine, forming $C_{10}H_{16}OBr_2$, easily converted into $C_{10}H_{15}BrO$.

Camphor treated with hypochlorous acid, yields *monochloro-camphor*, $C_{10}H_{15}ClO$, a crystalline mass melting at 95° and converted by heating with alcoholic potash into *oxycamphor*, $C_{10}H_{16}O_2$, which sublimes in needles melting at 137°. Camphor heated with PCl_5 yields the compounds $C_{10}H_{16}Cl_2$ and $C_{10}H_{15}Cl$, easily converted, by abstraction of hydrogen chloride, into cymene.

A solution of camphor in toluene heated with sodium, deposits a mixture of sodium-camphor and sodium-borneol:

$$2C_{10}H_{16}O + Na_2 = C_{10}H_{15}NaO + C_{10}H_{17}NaO;$$

and these compounds treated with CH_3I and C_2H_5I, yield methyl- and ethyl-derivatives of camphor and borneol; $C_{10}H_{15}(C_2H_5)O$ is a liquid boiling at 230°.

When the sodium-compounds are treated at 100° with CO_2, the sodium-salts of camphocarbonic acid, $C_{10}H_{15}O.CO_2H$, and borneocarbonic acid, $C_{10}H_{17}O.CO_2H$, are produced; and on treating the resulting mass with water, borneol separates from the toluene which floats on the surface, and the aqueous solution mixed with hydrochloric acid yields a precipitate of camphocarbonic acid. This acid crystallises from alcohol in small prisms, melting at 118°, and is easily resolved into CO_2 and camphor.

Isomerides of Camphor.—By distilling the essential oil of feverfew (*Pyrethrum Parthenium*), and collecting apart the portion which passes over between 200° and 220°, an oil is obtained, which, on cooling, deposits a crystalline substance resembling common camphor in every respect, except that its action on polarised light is exactly equal and opposite: $[\alpha] = -47{\cdot}4°$. The essential oils of many labiate plants, as rosemary, marjoram, lavender, and sage, often deposit a substance having the composition and all the properties of common camphor, excepting that it is inactive to polarised light.

Absinthol, $C_{10}H_{16}O$, from oil of wormwood (*Artemisia Absinthium*), is liquid, boils at 195°, and is converted by P_2S_5 into cymene. Similar liquid camphors are obtained by oxidation of certain terpenes, as the oils of orange and nutmeg. A polymeric camphor, caryophyllin, $C_{20}H_{32}O_2$ (m.p. above 300°), is contained in cloves.

Borneo-camphor or Borneol, $C_{10}H_{18}O = C_{10}H_{17}.OH$, occurs in *Dryabalanops Camphora*, a tree growing in Borneo and Sumatra: it is formed artificially by heating common camphor with alcoholic potash, or treating it with sodium (p. 599).

Borneol is very much like common camphor, has a camphorous and peppery odour, melts at 198°, and boils at 212°. Its alcoholic solution is dextrorotatory. By heating with nitric acid it is converted, first into common camphor, then into camphoric and camphoronic acids. By heating with P_2O_5, it is resolved into water and borneene, $C_{10}H_{16}$, apparently identical with the terpene contained in ordinary camphor-oil (from *Laurus Camphora*), and in valerian oil; when left in contact with potash-ley, it is reconverted into borneol.

Borneol is an alcohol, yielding compound ethers when heated to about 200° with organic acids. The *stearic ether*, $C_{10}H_{17}.O.C_{18}H_{35}O$, is a colourless, viscid liquid, which gradually solidifies. By the action of PCl_5 at ordinary temperatures, or by heating in a sealed tube with HCl, borneol is converted into the *chloride*, $C_{10}H_{17}Cl$, a crystalline substance melting at 146°, and very much like the solid modification of the hydrochloride of turpentine-oil, with which it is isomeric.

Isomeric with borneol are the liquid camphors contained in the oils of hops, Indian geranium, cajeput, coriander, and *Osmitopsis asteriscoïdes.* Homologous with borneol is *Patchouli-camphor*, $C_{15}H_{28}O$, contained in oil of patchouli: it is a crystalline mass, melting at 54°–55°, boiling at 296°.

Mint-camphor or **Menthol**, $C_{10}H_{20}O$, occurs, together with a terpene, in oil of peppermint (*Mentha piperita*), and separates in crystals on cooling the oil. It melts at 36°, boils at 213°; turns the plane of polarisation to the left; forms compound ethers with acids; is converted by PCl_5 or HCl into the liquid chloride, $C_{10}H_{19}Cl$, and by distillation with P_2O_5 or $ZnCl_2$ into liquid menthene, $C_{10}H_{18}$, which boils at 163°.

Acids produced by Oxidation of Camphor.

Campholic Acid, $C_{10}H_{18}O_2$, obtained by passing camphor-vapour over heated soda-lime, or by the action of potassium on a solution of camphor in petroleum, crystallises from alcohol in prisms or scales, slightly soluble in water, melting at 95°, and easily subliming; converted by nitric acid into camphoric and camphoronic acids; resolved by distillation with phosphoric anhydride into H_2O, CO_2, and campholene, C_9H_{12}, boiling at 135°.

Camphoric Acid, $C_{10}H_{16}O_4 = C_8H_{14}(CO_2H)_2$, is obtained by prolonged boiling of common camphor or borneol with nitric acid:

$$C_{10}H_{16}O + O_3 = C_{10}H_{16}O_4 \text{ and } C_{10}H_{18}O + O_4 = C_{10}H_{10}O_4 + H_2O.$$

It is dextro- or levo-rotatory according to the variety of camphor used in its preparation; a mixture of the dextro- and levo-rotatory camphors in equal quantities yields an inactive camphoric acid.

Dextrocamphoric acid crystallises from hot water in colourless laminæ, easily soluble in alcohol, melting at 175°–178°, and decomposing at a high temperature into water and camphoric anhydride,

$C_{10}H_{14}O_3$, which sublimes at 130° in shining needles, melts at 217°, and boils at 270°.

The acid is bibasic. The calcium and barium salts are easily soluble in water, and crystallise well. The calcium salt is resolved by heat into carbonate and camphor-phorone: $C_{10}H_{14}O_4Ca = CO_3Ca + C_9H_{14}O$, isomeric with phorone from acetone (p. 263), a liquid which boils at 208°, and does not yield cymene when heated with phosphoric anhydride.

Camphoric acid heated with water to 150°–200° is converted into two inactive modifications, isocamphoric and paracamphoric acids. The former crystallises in slender needles melting at 113°.

The acid, or its anhydride, heated with bromine to 130°–150°, yields *bromocamphoric anhydride*, $C_{10}H_{13}BrO_3$, which crystallises in needles melting at 215°, and, when boiled with water, is converted into the monobasic acid, $C_{10}H_{14}O_4$ (*oxycamphoric anhydride* or *camphanic acid*), melting at 201°, and subliming at 110°. This acid, or oxyanhydride, heated with water to 181°, yields a hydrocarbon C_8H_{14}, boiling at 120°.

Camphoronic acid, $C_9H_{12}O_5$, and Oxycamphoronic acid, $C_9H_{12}O_6$, are contained in the mother-liquor of the preparation of camphoric acid. The former crystallises from water in slender needles with 1 mol. H_2O, which it gives off at 110°; melts in the dehydrated state at 115°; and distils without decomposition. The oxyacid, $C_9H_{12}O_6$, crystallises in long prisms melting at 164·5°.

Resins and Balsams.

Common resin, or *colophony*, is perhaps the best example of the class. It is the resinous substance which remains when turpentine or pine-resin is heated till the water and volatile oil are expelled, and consists essentially of sylvic or abietic acid, $C_{20}H_{30}O_2$. On boiling the resin for a long time with alcohol of about 80 per cent., filtering, and adding a little water, the sylvic acid separates in the crystalline state. It crystallises from alcohol in laminæ melting at 129°. It is monobasic; its alkali-salts are soluble and crystallisable.

An acid called pimaric acid, isomeric with sylvic acid, is obtained from the turpentine of the *Pinus maritima* of Bordeaux.

Lac is a very valuable resin, much harder than colophony, and easily soluble in alcohol: three varieties are known in commerce —viz., *stick-lac*, *seed-lac*, and *shellac*. It is used in varnishes, and in the manufacture of hats, and very largely in the preparation of sealing-wax, of which it forms the chief ingredient. Crude lac contains a red dye called *lac-dye*, which is partly soluble in water. Lac dissolves in considerable quantity in a hot solution of borax; Indian ink, rubbed up with this liquid, forms an excellent *label-ink* for the laboratory, as it is unaffected by acid vapours, and, when once dry, becomes nearly insoluble in water.

Mastic, *dammar-resin*, and *sandarac* are resins largely used by the varnish maker. *Dragon's blood* is a resin of a deep red-colour. *Copal* is also a very valuable substance : it differs from the other resins in being but slowly dissolved by alcohol and essential oils. It is miscible, however, in the melted state with oils, and is thus made into varnish. *Amber* appears to be a fossil resin : it is found accompanying brown-coal or lignite.

Most resins, when exposed to destructive distillation, yield oily pyro-products, usually consisting of hydrocarbons.

Caoutchouc, or India-rubber, the thickened milky juice of several species of *Ficus*, *Euphorbia*, and other trees growing in tropical countries, is essentially a mixture of several hydrocarbons isomeric or polymeric with turpentine oil. When pure it is nearly white, the dark colour of commercial caoutchouc being due to the effects of smoke and other impurities. It is softened but not dissolved by boiling water : it is also insoluble in alcohol. In pure ether, rectified petroleum, and coal-tar oil, it dissolves, and is left unchanged on the evaporation of the solvent. Oil of turpentine also dissolves it, forming a viscid, adhesive mass, which dries very imperfectly. At a temperature a little above the boiling point of water, caoutchouc melts, but never afterwards returns to its former elastic state. Few chemical agents affect this substance : hence its great use in chemical investigations, for connecting apparatus, &c. By destructive distillation it yields a large quantity of a thin, volatile, oily liquid, of naphtha-like odour, called *caoutchoucin*, which dissolves caoutchouc with facility. This oil, according to Mr. Greville Williams, is composed of two polymeric hydrocarbons : caoutchin, $C_{10}H_{16}$, boiling at 171°, and isoprene, C_5H_8, boiling at 37°.

Caoutchouc combines with variable proportions of sulphur. The mixtures thus obtained are called *vulcanised India-rubber* : they are more permanently elastic than pure caoutchouc.

Vulcanite, or *Ebonite*, is caoutchouc mixed with half its weight of sulphur, and hardened by pressure and heating. It is very hard, takes a high polish, and is used for making combs, knife-handles, buttons, &c. It is also especially distinguished by the large quantity of electricity which it evolves when rubbed: hence it makes an excellent material for the plates of electrical machines.

Gutta-percha, the hardened milky juice of *Isonandra gutta*, a large tree growing in Malacca and many of the islands of the Eastern Archipelago, is similar in composition to caoutchouc, and resembles it in many of its properties, but is harder and less elastic. It is quite insoluble in, and impervious to water, and being also an excellent electric insulator, is extensively used as a casing for submarine telegraph wires. By dry distillation it yields isoprene, caoutchin, and a heavy oil called *heveene*, probably polymeric with these bodies.

Balsams are natural mixtures of resins with volatile oils. They differ very greatly in consistence, some being quite fluid, others solid and brittle. By keeping, the softer kinds often become hard.

Balsams may be conveniently divided into two classes—viz., those which, like *common* and *Venice turpentine, Canada balsam, Copaiba balsam*, &c., are merely natural varnishes, or solutions of resins in volatile oils, and those which contain benzoic or cinnamic acid in addition, as *Peru* and *Tolu balsams*, and the solid resinous *benzoin*, commonly called *gum-benzoin* (p. 531).

Glucosides.

This name is given to a class of bodies, very widely diffused in the vegetable kingdom, which are resolved by boiling with dilute acids or alkalis, or by the action of ferments, into glucoses (mostly dextrose), and some other substance. They are therefore analogous in constitution to the artificial glucosides which Berthelot obtained by heating glucose with organic acids (p. 196); none of them have, however, been formed artificially. The following are the most important :—

Æsculin, $C_{21}H_{24}O_{13}$, is a crystalline fluorescent substance obtained from the bark of the horse-chestnut and other trees of the genera *Æsculus* and *Pavia*. It has a bitter taste, is slightly soluble in water and alcohol, more soluble in the same liquids at the boiling heat, nearly insoluble in ether. It is coloured red by chlorine. By boiling with hydrochloric or dilute sulphuric acid, it is resolved into glucose and a bitter crystalline substance called æsculetin, $C_9H_6O_4$:

$$C_{21}H_{24}O_{13} + 3H_2O = 2C_6H_{12}O_6 + C_9H_6O_4.$$

The aqueous solution of æsculin is highly fluorescent, the reflected light being of a sky-blue colour. Nearly the same fluorescent tint is exhibited by an infusion of horse-chestnut bark. The colour of the latter is, however, slightly modified by the presence of another substance, paviin, which exhibits a blue-green fluorescence; it may be separated from æsculin by its greater solubility in ether. Æsculin and paviin appear to exist together in the barks of all species of *Æsculus* and *Pavia*,—æsculin being more abundant in the former, and paviin in the latter.

Amygdalin, $C_{20}H_{27}NO_{11}$, is a crystalline body existing in bitter almonds, the leaves of the cherry-laurel (*Cerasus Laurocerasus*), and many other plants which by distillation yield hydrocyanic acid and bitter-almond oil, C_7H_6O. To prepare it, the almonds, previously freed from fixed oil by pressure, are exhausted with boiling alcohol, and the concentrated solution is mixed with ether.

Amygdalin crystallises from alcohol in white shining laminæ, has a bitter taste, dissolves easily in water and in hot alcohol; from water it crystallises in prisms containing $3H_2O$.

By boiling with dilute acids, and by contact with water and emulsin or synaptase, a ferment contained in bitter almonds, amygdalin is resolved into bitter almond oil, glucose, and hydrocyanic acid:

$$C_{26}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

When amygdalin is boiled with alkalis, its nitrogen is separated as ammonia, and amygdalic acid, $C_{20}H_{28}O_{13}$, is formed, which by boiling with dilute acids is resolved into mandelic acid and glucose.

Arbutin, $C_{12}H_{16}O_7$, from the leaves of the bear-berry (*Arbutus uva ursi*), crystallises in slender needles, having a bitter taste, and dissolving easily in water, alcohol, and ether. By boiling with dilute acids it is resolved into glucose and hydroquinone:

$$C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2.$$

It dissolves in strong nitric acid, forming $C_{12}H_{14}(NO_2)_2O_7$, which splits up into glucose and dinitrohydroquinone.

Chitin, $C_9H_{15}NO_6$, is the substance which forms the elytra and integuments of insects, and the carapaces of crustaceans. It is best prepared by boiling the wing-cases of cockchafers with water, alcohol, ether, acetic acid, and alkalis in succession, as long as anything is dissolved out by each. According to Städeler, it is resolved by boiling with dilute acids into glucose and lactamide, $C_3H_7NO_2$:

$$C_9H_{15}NO_6 + 2H_2O = C_6H_{12}O_6 + C_3H_7NO_2.$$

Coniferin, $C_{16}H_{22}O_8$, occurs in the cambial juice of coniferous plants, and separates therefrom on concentration in stellate groups of pointed needles, having a satiny lustre, and containing $2H_2O$, which they lose by efflorescence. By boiling with dilute acids it is resolved into dextrose and a resin; in contact with emulsin, into dextrose and coniferyl alcohol. By oxidation with chromic acid mixture it yields vanillin (p. 512).

Convolvulin, $C_{31}H_{50}O_{16}$, is obtained from jalap root (*Convolulus schiedanus*) by extraction with alcohol. It is a gummy mass having a strong purgative action; dissolves in alkalis as convolvulic acid, $C_{31}H_{52}O_{17}$; resolved by acids and by emulsin into dextrose and convolvulinol, $C_{13}H_{24}O_3$, which is converted by alkalis into convolvulinolic acid, $C_{13}H_{26}O_4$. This latter is a monobasic acid, which is oxidised by nitric acid to ipomæic acid, $C_{16}H_{18}O_4 = C_8H_{16}(CO_2H)_2$, isomeric with sebacic acid (p. 351).

Jalappin, $C_{34}H_{56}O_{16}$, from the root of *Convolvulus orizabensis*, closely resembles convolvulin, and yields analogous products of decomposition.

Glycyrrhizin, $C_{24}H_{36}O_9$; *Liquorice-sugar.*—The root of the common liquorice yields a large quantity of a peculiar sweet substance, which is soluble in water, but does not crystallise: it cannot be made to ferment. Glycyrrhizin forms difficultly soluble compounds with acids; it is precipitated from its solution by lead, calcium, and barium salts, the precipitate consisting of glycyrrhizin in combination with the base. When boiled with dilute acids, it splits into a resinous body called glycyrretin, $C_{18}H_{26}O_4$, and glucose:

$$C_{24}H_{36}O_9 + H_2O = C_{18}H_{26}O_4 + C_6H_{12}O_6 .$$

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, an acid existing as a potassium salt in the seed of black mustard, is resolved by the action of *myrosin*, an albuminous ferment likewise contained in the seeds, into volatile oil of mustard (allyl sulphocyanate), glucose and sulphuric acid:

$$C_{10}H_{18}KNS_2O_{10} = C_3H_5.CNS + C_6H_{12}O_6 + SO_4HK .$$

Phlorizin, $C_{21}H_{24}O_{10}.2H_2O$, is a substance bearing a great likeness to salicin, found in the root-bark of the apple and cherry-tree, and extracted by boiling alcohol. It forms fine, colourless, silky needles, soluble in 1000 parts of cold water, but freely dissolved by that liquid when hot; it also dissolves easily in alcohol. Dilute acids convert phlorizin into glucose and a crystallisable sweet substance called phloretin:

$$C_{21}H_{24}O_{10} + H_2O = C_6H_{12}O_6 + C_{15}H_{14}O_5 .$$

Phlorizin, fused with potash, yields phloretic acid, $C_9H_{10}O_3$, a beautifully crystalline acid, homologous with salicylic and anisic acids, together with phloroglucin, $C_6H_6O_3$.

Quercitrin is a crystallisable yellow colouring matter occurring in quercitron bark, the bark of *Quercus infectoria*, whence it is extracted by boiling with water. Its composition has been variously stated; indeed it is by no neans certain that the so-called quercitrins examined by different chemists were really identical substances. According to Hlasiwetz and Pfaundler, it contains $C_{33}H_{30}O_{17}$, and is resolved by boiling with dilute acids into another yellow crystalline body called quercetin, and isodulcite (p. 190):

$$\underset{\text{Quercitrin.}}{C_{33}H_{30}O_{17}} + H_2O = \underset{\text{Quercetin.}}{C_{27}H_{18}O_{12}} + \underset{\text{Isodulcite.}}{C_6H_{14}O_6} .$$

Salicin, $C_{13}H_{18}O_7$, is a crystallisable bitter substance contained in the leaves and young bark of the poplar, willow, and several other trees. It may be prepared by exhausting the bark with boiling water, concentrating the solution to a small bulk, digesting the liquid with powdered lead oxide, and then, after freeing the solution from lead by a stream of sulphuretted hydrogen gas, evaporating till the salicin crystallises out on cooling. It is purified by treatment with animal charcoal and recrystallisation.

Salicin forms small, white silky needles, having an intensely bitter taste, but no alkaline reaction. It melts and decomposes by heat, burning with a bright flame, and leaving a residue of charcoal. It is soluble in 5·6 parts of cold water, and in a much smaller quantity when boiling hot. Oil of vitriol colours it deep red. When distilled with a mixture of potassium bichromate and sulphuric acid, it yields salicylal and other products.

Salicin, under the influence of the emulsin or synaptase of sweet almonds, is resolved into glucose and saligenin, $C_7H_8O_2$ (p. 505).

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2 .$$

Salicin yields, with *chlorine*, substitution-products which are decomposed by synaptase in the same manner as salicin itself, yielding chlorosaligenin, $C_7H_7ClO_2$, and dichlorosaligenin, $C_7H_6Cl_2O_2$. Dilute *nitric acid* converts salicin into helicin. With strong nitric acid, at a high temperature, nitrosalicylic acid, $C_7H_5(NO_2)O_3$, is produced.

Populin, $C_{20}H_{22}O_8$, is a substance resembling salicin in appearance and solubility, but having a sweet pungent taste. It is found accompanying salicin in the bark and leaves of the aspen. It has the composition of benzoyl-salicin, $C_{13}H_{17}(C_7H_5O)O_7$, and when heated with dilute acids, is resolved into benzoic acid and the products of decomposition of salicin, namely, saliretin and glucose:

$$C_{13}H_{17}(C_7H_5O)O_7 + H_2O = C_7H_6O_2 + C_7H_6O + C_6H_{12}O_6 .$$

With potassium dichromate and sulphuric acid, populin yields a considerable quantity of salicylal.

Helicin, $C_{13}H_{16}O_7$, is a white, crystalline, slightly bitter substance, produced by the action of very dilute nitric acid upon salicin:

$$C_{13}H_{18}O_7 + O = H_2O + C_{13}H_{16}O_7 .$$

It is slightly soluble in cold, freely soluble in boiling water, and is resolved by the action of synaptase, or of acids or alkalis at the boiling heat, into glucose and salicylal:

$$C_{13}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_7H_6O_2 .$$

Benzohelicin, $C_{20}H_{20}O_8$, or $C_{13}H_{15}(C_7H_5O)O_7$, produced by the action of dilute nitric acid on benzo-salicin, is resolved in like manner into benzoic acid, salicylal, and glucose:

$$C_{20}H_{20}O_8 + 2H_2O = C_7H_6O_2 + C_7H_6O_2 + C_6H_{12}O_6 .$$

Bitter Principles of Plants.

These are neutral bodies of somewhat indefinite chemical character, which cannot at present be included in any of the preceding groups.

Aloïn is a constituent of aloes, the inspissated juice of various species of aloe, and is extracted by treating the aloes with water. It is easily soluble in warm water and alcohol, and crystallises in slender needles. It is very bitter and strongly purgative.

Aloïn from Barbadoes aloes has the composition $C_{17}H_{18}O_7$; that from Natal aloes is $C_{34}H_{38}O_{15} = 2C_{17}H_{18}O_7 + H_2O$. The former (barbaloïn) heated with nitric acid yields aloetic acid $C_{14}H_4(NO_2)_4O_2$ together with oxalic, picric and chrysammic acids; the latter (nataloïn) yields picric and oxalic acids, but no chrysammic acid.

Athamantin, $C_{24}H_{30}O_7$, obtained from the roots of *Athamanta Oreoselinum* by extraction with ether, crystallises from alcohol and ether in slender needles melting at 79°. By boiling with hydrochloric acid it is resolved into valeric acid and oreoselone, $C_{14}H_{10}O_3$:

$$C_{24}H_{30}O_7 = 2C_5H_{10}O_2 + C_{14}H_{10}O_3.$$

By further boiling with dilute hydrochloric acid, oreoselone is converted into oreoselin, $C_{14}H_{12}O_4$.

Cantharidin, $C_5H_0O_2$, is the vesiccating principle of Spanish flies and some other insects, and may be extracted with ether. It crystallises in four-sided prisms or laminæ, dissolves in hot alcohol and ether, melts at 250°, and sublimes at a lower temperature. Heated with alkalis it dissolves, forming salts of cantharidic acid, *e.g.*, $C_5H_7KO_3$, from which acids reprecipitate cantharidin.

Carotin, $C_{18}H_{24}O$, a substance deposited in small crystals in the cells of the red carrot, crystallises from alcohol in red-brown cubes melting at 168°.

Peucedanin, $C_{24}H_{24}O_6$, from the roots of *Peucedanum officinale*, crystallises from alcohol in shining prisms melting at 75°. Boiled with alcoholic potash it is resolved into angelic acid and oreoselin.

Picrotoxin, $C_{12}H_{14}O_6$, is extracted by alcohol from cocculus grains (the seeds of *Menispermum Cocculus*); crystallises in slender needles; very bittter and poisonous.

Santonin, $C_{15}H_{18}O_3$, is the active principle of wormseed (from *Artemisia santonica*), from which it may be extracted by boiling with milk of lime and precipitation by hydrochloric acid. It crystallises from hot alcohol in shining prisms melting at 170°; dissolves in alkalis, forming salts of santoninic acid, $C_{15}H_{20}O_4$.

Colouring Matters.

The most important colouring matters of vegetable origin, viz., the indigo and madder dyes, have already been described.

Brazilin, $C_{22}H_{18}O_7$, the colouring matter of Brazil wood, crystallises in small yellow prisms, which dissolve in alcohol with reddish yellow, in alkalis with crimson colour; the solution is decolorised by sulphurous acid and zinc-dust. Nitric acid converts brazilin into trinitroresorcin.

Carminic acid, $C_{17}H_{18}O_{10}$, occurs in the flowers of *Monarda didyma* and a few other plants, and more abundantly in cochineal, an insect (*Coccus Cacti*) living on various species of cactus. To obtain the carminic acid, the aqueous decoction of the insects is precipitated by lead acetate, and the pure lead carminate washed and decomposed by hydrogen sulphide; the colouring matter thus separated is again submitted to the same treatment. A solution of carminic acid is thus obtained, which is evaporated to dryness, redissolved in absolute alcohol, digested with crude lead carbonate, whereby a small quantity of phosphoric acid is separated, and lastly, mixed with ether, which separates a trace of a nitrogenous substance. The residue now obtained on evaporation is pure carminic acid.

It is a purple-brown mass, yielding a fine red powder, soluble in water and alcohol in all proportions, slightly soluble in ether. It dissolves without decomposition in concentrated sulphuric acid, but is readily attacked by chlorine, bromine, and iodine, which change its colour to yellow. It resists a temperature of 136°, but is charred when heated more strongly. Carminic acid is bibasic, and forms coloured salts. By boiling with dilute sulphuric acid it is resolved into a non-fermentable sugar and carmine-red, $C_{11}H_{12}O_7$. Boiled with nitric acid it yields oxalic acid and nitrococcusic acid, $C_8H_5(NO_2)_3O_3.H_2O$, which crystallises from water in large shining plates, and when heated with water to 180° is resolved into CO_2 and trinitro-cresotic acid, $C_6(NO_2)_3(CH_3)(OH).CO_2H$. Cochineal is used for giving a red colour to silk and wool.

Carthamin, $C_{14}H_{16}O_7$, is the red colouring matter of the petals of the safflower (*Carthamus tinctorius*). It is prepared by exhausting the flowers with cold water to remove a yellow substance, and treating the residue with a dilute solution of sodium carbonate; this dissolves the carthamin, which may be precipitated by acetic acid as a dark red powder having a green metallic lustre when dry. It dissolves in alcohol and alkalis with a fine red colour, which, however, is very fugitive. By fusion with potash it yields paraoxybenzoic and oxalic acids. Carthamin is used for dyeing silk, and as a cosmetic.

Chlorophyll, or Leaf-green, is contained, together with wax and other substances, in the chlorophyll granules which occur in all the green parts of plants, and may be obtained by exhausting these organs with ether, and treating the residue with alcohol, in which the chlorophyll is easily soluble. It dissolves also in strong hydrochloric acid. Its composition is not known, but iron appears to be an essential constituent.

Curcumin, $C_{10}H_{16}O_3$, is the colouring matter of turmeric. It dissolves easily in alcohol and ether, sparingly in carbon sulphide, and in cold benzene, and is best extracted from the root by boiling benzene. It forms orange-yellow crystals, and exhibits in solution a green fluorescence. From its brown-red solution in alkalis, it is precipitated by acids as a yellow powder. The yellow tint of paper stained with turmeric is turned brown by alkalis and restored by acids.

Euxanthic acid, $C_{19}H_{16}O_{10}$, occurs as a magnesium salt in *Purree* or *Indian yellow*, a yellow colouring matter of unknown origin imported from India and China. The euxanthic acid is obtained by digesting the mass with dilute hydrochloric acid, and exhausting with alcohol. It dissolves easily in alcohol and ether, and crystallises in shining yellow prisms. Euxanthic acid is resolved by strong sulphuric acid into a saccharine substance and euxanthone, $C_{13}H_8O_4$, which sublimes in yellow needles. Euxanthone fused with potash yields first euxanthonic acid, $C_{13}H_{10}O_5$, then hydroquinone. Strong nitric acid converts it into trinitroresorcin, and, on the other hand, resorcin heated with oxalic and sulphuric acid, appears to yield euxanthone.

Hematoxylin, $C_{16}H_{14}O_6$, the colouring matter of logwood, crystallises with 3 mol. H_2O in pale-yellow prisms; has a sweetish taste; dissolves easily in water, alcohol, and ether, forming dextro-rotatory solutions. With *acetyl chloride*, it forms $C_{16}H_8(C_2H_3O)_6O_6$. By exposure to the air in ammoniacal solution, it is converted into hematein-ammonia, $C_{16}H_{11}(NH_4)O_6$, which, on spontaneous evaporation, is deposited in dark violet crystals. Acetic acid added to the solution throws down hematein, $C_{16}H_{13}O_6$, as a red-brown precipitate, having a metallic lustre when dry, and dissolving in alkalis with a fine violet-blue colour. Sulphurous acid and other reducing agents reconvert hematein into hematoxylin. The latter, fused with potash, yields pyrogallol.

Alkaloïds.

This term is sometimes used as a general name for organic bases, but it is more especially applied to those which occur ready formed in the bodies of plants and animals, and those which are produced by the destructive distillation of complex organic bodies. All these bases, like the amines already described, are derivatives of ammonia, but their molecular structure is for the most part unknown. Those which are free from oxygen are volatile; those which contain that element are decomposed by distillation.

NON-OXIDISED VOLATILE BASES.

Pyridine Bases, $C_nH_{2n-5}N$.—These bases, metameric with aniline and its homologues, are contained in coal-tar naphtha, and in the volatile oil called Dippel's oil (*Oleum animale Dippelii*), obtained by the distillation of bones and other animal matters. They are all liquid at ordinary temperatures, and react as tertiary monamines. Their formulæ and boiling points are as follows:—

		B.P.			B.P.
Pyridine,	C_5H_5N,	117	Parvoline,	$C_9H_{13}N$,	188°
Picoline,	C_6H_7N,	133°	Coridine,	$C_{10}H_{15}N$,	211°
Lutidine,	C_7H_9N,	154°	Rubidine,	$C_{11}H_{17}N$,	230°
Collidine,	$C_8H_{11}N$,	179°	Viridine,	$C_{12}H_{19}N$,	251°

Pyridine is said to be formed artificially by heating amyl nitrate with phosphoric oxide: $C_5H_{11}NO_3 - 3H_2O = C_5H_5N$. When heated with sodium it is converted into dipyridine, $C_{10}H_{10}N_2$, a crystalline base which melts at 108°, and sublimes at higher temperatures in needle-shaped crystals.

Picoline (metameric with aniline), first obtained by Anderson from coal-tar naphtha, is a mobile liquid, having a strong, persistent odour, and acrid, bitter taste: sp. gr. 0·955. It remains liquid at −18°, and volatilises quickly in the air. It is strongly alkaline to test-paper, mixes with water in all proportions, and forms crystallisable salts.

Dippel's oil likewise contains methylamine and several of its homologues.

Chinoline Bases, $C_nH_{2n-11}N$.—Three bases of this series, viz.:

C_9H_7N	$C_{10}H_9N$	$C_{11}H_{11}N$
Chinoline.	Lepidine.	Cryptidine.

are produced by distillation of quinine, cinchonine, and a few other natural alkaloïds, with potassium hydroxide; and other bases isomeric with them, viz., *leucoline*, C_9H_7N, *iridoline*, $C_{10}H_9N$, &c., are contained in coal-tar naphtha, and distil over after the pyridine bases (above 200°). They are oily liquids insoluble in water, easily soluble in alcohol and ether. They are tertiary amines, yielding ammonium-bases when treated with ethyl iodide and silver oxide. These salts are crystalline, and easily soluble.

Chinoline, C_9H_7N, is a mobile, strongly refracting liquid, boiling at 238°, and having a sp. gr. of 1·081 at 0°. Heated with amyl iodide, it forms the compound $(C_9H_7)(C_5H_{11})NI$, which is converted by heating with potash into cyanine, $C_{28}H_{25}NI$, a fine blue dyestuff, which crystallises in green metallically lustrous plates, and dissolves with blue colour in alcohol. A similar blue colour is obtained with lepidine, and a mixture of the two has been used for dyeing silk.

Leucoline, C_9H_7N, from coal-tar oil, boils at about 220°, and does not yield cyanine.

Lepidine, from cinchonine, boils at 266°–270°; the isomeric base from coal-tar boils at 252°–257°.

Conine, $C_8H_{15}N$, is contained in hemlock (*Conium muculatum*), especially in the seeds, and is obtained therefrom by distillation with potash-ley. It is a colourless oily liquid, having a pungent, stupefying odour, and is very poisonous. Sp. gr. 0·89. Boiling point 168°. It dissolves easily in alcohol and ether, sparingly in water, and forms crystalline deliquescent salts, which, like the base itself, turn brown in contact with the air. With oxidising agents conine yields butyric acid.

Conine is a secondary monamine. Treated with ethyl iodide it yields successively two iodine-compounds—namely, $C_8H_{15}(C_2H_5)NI$ and $C_8H_{14}(C_2H_5)_2NI$. The latter is converted by silver oxide into a soluble base.

Paraconine, isomeric with conine, is formed artificially by heating normal butyric aldehyde, C_4H_8O, with alcoholic ammonia,—whereby *dibutyraldine* is obtained, having the composition $C_8H_{17}NO$ $[=2C_4H_8O+NH_3-H_2O]$,—and subjecting this base to dry distillation: $C_8H_{17}NO-H_2O=C_8H_{15}N$. It is a violent poison, acting in the same manner as the natural base. But it is less soluble in water, more expansible by heat, and exhibits somewhat different reactions with hydrochloric acid, silver nitrate, and gold chloride. With ethyl iodide it forms the iodide of an ammonium-base, convertible by silver oxide into a strongly alkaline, bitter syrupy liquid: hence it is a tertiary monamine.

Closely allied to conine is *conhydrine*, $C_8H_{17}NO$, a crystalline base, extracted from hemlock flowers. When distilled with anhydrous phosphoric acid, it splits into conine and one molecule of water.

Nicotine, $C_{10}H_{14}N_2$, exists in the seeds and leaves of various kinds of tobacco, from which it may be obtained by extraction with dilute sulphuric acid, and distillation of the concentrated extract with potash-ley. It is a colourless oil, having a density of 1·048, boiling with partial decomposition at 250°, without decomposition in a stream of hydrogen at 150°-200°. It turns brown in the air, has a very stupefying odour, and is very poisonous. It is a monoacid base, forming very soluble salts, which crystallise with difficulty.

A mixture of nicotine with methyl or ethyl iodide solidifies after a short time to a crystalline mass, containing $C_{10}H_{14}(CH_3)_2N_2I_2$, or $C_{10}H_{14}(C_2H_5)_2N_2I_2$, convertible by silver oxide into soluble bases.

By fuming nitric acid or chromic acid mixture nicotine is oxidised to nicotic acid, $C_{10}H_8N_2O_3$, which, when distilled with lime, yields pyridine, and when heated with bromine-water to 120° is resolved into bromoform, carbon dioxide, nitrogen, and pyridine.

Sparteine, $C_{15}H_{26}N_2$, occurs in the common broom (*Spartium scoparium*), and is obtained therefrom by extraction with dilute sulphuric acid and distillation with potash. It is a colourless liquid, boiling at 228°; dissolves sparingly in water, has a bitter taste, and acts as a narcotic. It is strongly alkaline, and has the constitution of a biacid tertiary amine.

OXYGENISED BASES.

1. *Bases related to the Ureides.—Derivatives of Guanidine.*

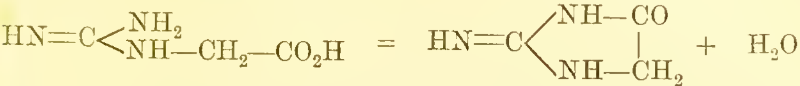
The following compounds are derived from guanidine $CH_5N_3 = HNC{=}(NH_2)_2$ (p. 226), by the substitution of acid radicles for an atom of hydrogen.

Glycocyamine or **Guanidacetylic Acid**, $C_3H_7N_3O_2$, is formed on mixing the aqueous solutions of glycocine and cynamide (p. 105):

$$\underset{\text{Cynamide.}}{HN{=}C{=}NH} + \underset{\text{Glycocine.}}{H_2C(NH_2)(CO_2H)} = \underset{\text{Glycocyamine.}}{HN{=}C(NH_2)(NH.CH_2.CO_2H)};$$

and separates in granular crystals, soluble in 120 parts of cold water, easily soluble in hot water, insoluble in alcohol and ether. It unites with bases forming crystalline compounds. Boiled with water and lead-oxide, or with dilute sulphuric acid, it is resolved into guanidine, oxalic acid and carbonic acid.

Glycocyamidine or **Glycolylguanidine**, $C_3H_5N_3O$, related to glycocyamine in the same manner as hydantoïn to hyrantoic acid (p. 410), is formed, as a hydrochloride, by heating the hydrochloride of glycocyamine to 160° :

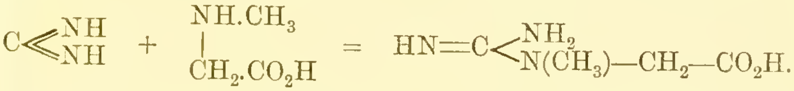


$$HN{=}C{<}\begin{matrix}NH_2\\ NH{-}CH_2{-}CO_2H\end{matrix} \quad = \quad HN{=}C{<}\begin{matrix}NH{-}CO\\ \quad |\\ NH{-}CH_2\end{matrix} \quad + \quad H_2O$$

Glycocyamine. Glycocyamidine.

The free base crystallises in deliquescent laminæ, having an alkaline reaction. Its hydrochloride gives a precipitate with platinic chloride.

Creatine, $C_4H_9N_3O_2$, *Methylglycocyamine*, occurs in the animal organism, especially in flesh juice, and is formed artificially, like glycocyamine, by the union of cyanamide with methyl-glycocine (sarcosine, p. 383) :

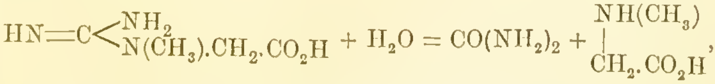


$$C{\ll}\begin{matrix}NH\\ NH\end{matrix} \quad + \quad \begin{matrix}NH.CH_3\\ |\\ CH_2.CO_2H\end{matrix} \quad = \quad HN{=}C{<}\begin{matrix}NH_2\\ N(CH_3){-}CH_2{-}CO_2H.\end{matrix}$$

It may be prepared by macerating finely chopped meat in cold water, boiling the extract to coagulate albumin, precipitating the phosphoric acid from the filtrate by baryta-water, and evaporating to the crystallising point.

Creatine crystallises in shining prisms containing 1 mol. H_2O, which they give off at 100°. It is neutral, slightly bitter, moderately soluble in boiling water, very sparingly in alcohol; forms crystalline salts containing one equivalent of acid.

Creatine heated with acids is converted, by abstraction of H_2O, into creatinine (*infra*). By boiling with water, it is resolved into urea and sarcosine :

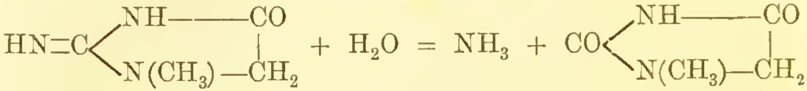


$$HN{=}C{<}\begin{matrix}NH_2\\ N(CH_3).CH_2.CO_2H\end{matrix} + H_2O = CO(NH_2)_2 + \begin{matrix}NH(CH_3)\\ |\\ CH_2.CO_2H\end{matrix},$$

methyl-hydantoïn being also formed, and ammonia given off. Boiled with mercuric oxide, it yields methylguanidine and oxalic acid.

Creatinine, $C_4H_7N_3O$, *Methylglycocyamidine*, is an almost constant constituent of urine (0·25 per cent.), and is formed from creatine by evaporating the aqueous solution of the latter, especially in presence of acids. It crystallises in rhombic prisms, much more soluble in water and alcohol than creatine; expels ammonia from its salts; and forms well crystallised salts with acids. It unites also with certain salts, forming, for example, the compound $(C_4H_7N_3O)_2ZnCl_2$, which is precipitated by zinc chloride from solutions of creatinine as a sparingly soluble crystalline powder.

Creatinine is reconverted into creatine by the action of bases, and is resolved by boiling with baryta into ammonia and methyl-hydantoïn:



$$HN{=}C\left\langle\begin{array}{l}NH\text{———}CO\\ \qquad\qquad\ |\\ N(CH_3)\text{—}CH_2\end{array}\right. + H_2O = NH_3 + CO\left\langle\begin{array}{l}NH\text{———}CO\\ \qquad\qquad\ |\\ N(CH_3)\text{—}CH_2\end{array}\right.$$

By boiling with mercuric oxide it is resolved, like creatine, into methylguanidine and oxalic acid.

Nearly related to the ureides are also the bases guanine, sarcine, xanthine, and carnine, which, like urea, occur in the animal organism as products of the oxidation of the tissues,—and the two vegetable bases, theobromine and caffeine. The constitution of these bases is not yet established, but their relation to the ureides is shown by their products of decomposition.

Guanine, $C_5H_5N_5O$, was first obtained from guano; it has also been proved to exist in the pancreatic juice of mammalia, and in the excrement of the spider. To prepare it, guano is boiled with water and calcium hydrate until a portion of the liquid, when filtered, appears but slightly coloured: the whole is then filtered, and the filtrate saturated with acetic acid, whereby the guanine is precipitated, mixed with uric acid. It is purified by solution in hydrochloric acid and precipitation by ammonia.

Guanine is a colourless, crystalline powder, insoluble in water, alcohol, ether, and ammonia, soluble in acids and solution of potash. It unites with acids forming crystallisable salts, *e.g.*, $C_5H_5N_5O.HCl + aq.$; $2C_5H_5N_5O.H_2SO_4 + 2\ aq.$; $3C_5H_5N_5O.2C_2H_2O_4$; also with metallic bases and salts; *e.g.*, $C_5H_5N_5O.NaHO + 2\ aq.$; $C_5H_5N_5O.AgNO_3$. By oxidation with hydrochloric acid and potassium chlorate, it is converted into a mixture of guanidine and parabanic acid (407).

Xanthine, $C_5H_4N_4O_2$, is found in small quantity in many animal secretions, as in urine and blood, in the liver, and in certain urinary calculi; it is formed artificially by the action of nitrous acid upon guanine, and of sodium amalgam on uric acid. It is a white amorphous mass, somewhat soluble in boiling water, and uniting both with acids and with bases. It dissolves easily in boiling aqueous ammonia, and silver-nitrate added to the solution throws down the compound $C_5H_2Ag_2N_4O_2 + H_2O$. This compound treated with methyl iodide yields a body isomeric with theobromine:

$$C_5H_2Ag_2N_4O_2 + 2CH_3I = 2AgI + C_7H_8N_4O_2.$$

Sarcine or **Hypoxanthine,** $C_5H_4N_4O$, almost always accompanies xanthine in the animal organism; and is distinguished from xanthine especially by the sparing solubility of its hydrochloride. It forms needles slightly soluble in water, more soluble in acids and alkalis. From its ammoniacal solution, silver nitrate throws down the compound $C_5H_2Ag_2N_4O + H_2O$.

Carnine, $C_7H_8N_4O_3$, occurs in extract of meat. It is pulverulent, moderately soluble in hot water, and forms a crystalline hydrochloride.

Theobromine, $C_7H_8N_4O_2$, which differs in composition from carnine by only 1 atom of oxygen, occurs in cacao beans, the seeds of *Theobroma Cacao*, from which cocoa and chocolate are prepared. To extract it, the beans are boiled with water; the solution is precipitated with lead acetate, to remove extraneous matters; the filtrate is freed from lead by hydrogen sulphide, and evaporated to dryness; and the residue is treated with alcohol, which extracts the theobromine.

Theobromine is a white crystalline powder, having a bitter taste, slightly soluble in water and in alcohol, moderately soluble in aqueous ammonia. It has a neutral reaction, but unites with acids, forming crystalline salts, which are decomposed by water. From the ammoniacal solution silver nitrate throws down the compound $C_7H_7AgN_4O_2$, which, by heating to 100° with methyl iodide, is converted into methyl-theobromine, $C_7H_7(CH_3)N_4O_2$, or theine.

Theine or **Caffeine,** $C_8H_{10}N_4O_2$, *Methyl-theobromine*, occurs in the leaves and seeds of the coffee-tree, in tea-leaves, in Paraguay tea (from *Ilex paraguayensis*), and in guarana, the dried pulp of the fruit of *Paullinia sorbilis*. Theine is extracted from these substances by the process above described for the preparation of theobromine: it crystallises on cooling, and may be purified by means of animal charcoal.

Theine forms tufts of silky needles containing 1 mol. H_2O, slightly soluble in cold water and in alcohol, and giving off their water of crystallisation at 100°. It melts at 225°, and sublimes without decomposition at a higher temperature. It is a weak base, most of its salts being decomposed by water. The aurochloride and platinochloride, however, are more stable, and form orange-yellow crystals.

By the action of chlorine or nitric acid, theine is converted, with evolution of methylamine and cyanogen chloride, into amalic acid, $C_{12}H_{12}N_4O_7$, which has the composition of tetramethyl-alloxantin, $C_8(CH_3)_4N_4O_7$. It forms sparingly soluble crystals, which are coloured violet-blue by alkalis. By the further action of chlorine-water, theine yields cholestrophane or dimethyl-parabanic-acid, $C_3(CH_3)_2N_2O_3$ (p. 408).

Theine boiled with baryta-water, is resolved into CO_2, and theidine or caffeidine, $C_7H_{12}N_4O$, an easily soluble strongly basic compound, which is decomposed by prolonged boiling with water into sarcosine and other products.

2. *Opium Bases.*

Opium, the inspissated juice of the half-ripe capsules of the poppy (*Papaver somniferum*), is a very complex substance, containing a large number of bases combined with sulphuric and meconic acid. The best known of these bases are—

Morphine,*	$C_{17}H_{19}NO_3$	Papaverine,	$C_{21}H_{21}NO_4$
Codeine,	$C_{18}H_{21}NO_3$	Narcotine,	$C_{22}H_{23}NO_7$
Thebaine,	$C_{19}H_{21}NO_3$	Narceine,	$C_{23}H_{29}NO_4$

Of these, morphine and narcotine are the most abundant, the rest occurring in small quantity, and only in particular varieties of opium.

The bases are obtained by digesting opium with warm water, precipitating the meconic acid with calcium chloride, and leaving the concentrated filtrate to crystallise. The hydrochlorides of morphine and codeine then crystallise out first, and may be separated by treating their aqueous solution with ammonia, whereby the morphine is alone precipitated, the codeine remaining dissolved.

The mother-liquor of the morphine and codeine hydrochlorides is mixed with ammonia, which throws down narcotine, together with small quantities of papaverine, and thebaine, and a resin, while narceine remains in solution.

Morphine, $C_{19}H_{19}NO_3 + H_2O$, *Morphia* or *Morphium*, is precipitated from its salts as a white powder, and crystallises from alcohol in small but very brilliant prisms. It requires at least 500 parts of water for solution, tastes slightly bitter, and has an alkaline reaction. These effects are much more evident in the alcoholic solution. It dissolves in about 30 parts of boiling alcohol, and with great facility in dilute acids; it is also dissolved by excess of caustic potash or soda, but scarcely by excess of ammonia. When heated in the air, morphine melts, burns like a resin, and leaves a small quantity of charcoal, which easily burns away. Morphine in small doses is narcotic; in larger doses, highly poisonous.

Morphine is a tertiary mono-acid base. Its *hydrochloride*, $C_{17}H_{19}NO_3.HCl + 3H_2O$, crystallises in tufts of slender needles easily soluble in water and in alcohol. The *acetate*, $C_{17}H_{19}NO_3.C_2H_4O_2$, is moderately soluble in water, and crystallises in needles.

Solutions of morphine and its salts are coloured dark blue by ferric chloride; its solution in strong sulphuric acid is coloured blood-red by a drop of nitric acid. Solution of iodine added to the solution of the hydrochloride throws down the periodide, $C_{17}H_{19}NO_3I_4$. Morphine heated with potash-ley gives off methylamine.

Apomorphine, $C_{17}H_{17}NO_2$, a compound containing $1H_2O$ less than morphine, is formed when morphine is heated in a sealed tube with strong hydrochloric acid, and separates as a white powder, which turns green in contact with the air. It differs from morphine in being soluble in alcohol, ether, and chloroform, and in its physiological action, which is not narcotic, but emetic.

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* It is convenient to designate organic bases by names ending in *ine;* neutral substances by names ending in *in; e.g., gelatin, albumin, casein.*

Codeine, $C_{18}H_{21}NO_3 = C_{17}H_{18}(CH_3)NO_3$, *Methyl-morphine.*—This base, obtained from opium as above described, crystallises from ether in large rhombic prisms melting at 120°. It is more soluble in water than the other opium bases; potash precipitates it from the solutions of its salts. Heated with soda-lime it gives off methylamine and trimethylamine. Heated with strong hydrochloric acid to 140°–150°, it is resolved into methyl chloride and apomorphine:

$$C_{18}H_{21}NO_3 + HCl = CH_3Cl + H_2O + C_{17}H_{17}NO_2 .$$

Codeine is also a tertiary monamine, forming with ethyl iodide a crystalline iodide, $C_{18}H_{21}(C_2H_5)NO_3.I$, converted by silver oxide into an alkaline base.

Narcotine, $C_{22}H_{23}NO_7$.—The *marc*, or insoluble portion of opium, contains much narcotine, which may be extracted by boiling with dilute acetic acid. From the filtered solution the narcotine is precipitated by ammonia, and afterwards purified by solution in boiling alcohol, and filtration through animal charcoal. Narcotine crystallises in small, colourless, brilliant prisms, nearly insoluble in water. Its basic powers are very feeble; it is destitute of alkaline reaction, and although freely soluble in acids, does not, for the most part, form crystallisable salts.

Narcotine, treated with a mixture of dilute sulphuric acid and manganese dioxide, or a hot solution of platinic chloride, yields opianic acid (p. 550), together with basic products.

Cotarnine, $C_{12}H_{13}NO_3$, is contained in the mother-liquor from which opianic acid has crystallised: it forms a yellow crystalline mass, very soluble, of bitter taste, and feebly alkaline reaction. Its hydrochloride is a well-defined salt.

Cotarnine, gently heated with very dilute nitric acid, is converted into methylamine nitrate, and *cotarnic acid*, a bibasic acid containing $C_{11}H_{12}O_5$:

$$C_{12}H_{13}NO_3 + 2H_2O + HNO_3 = CH_5N.HNO_3 + C_{11}H_{12}O_5 .$$

Thebaine, $C_{19}H_{21}NO_3$, *Papaverine*, $C_{20}H_{21}NO_4$, and *Narceine*, $C_{23}H_{29}NO_9$, are also contained in opium in small quantity. Thebaine forms silvery scales, melting at 193°; insoluble in water, potash, and ammonia. Papaverine melts at 141°–145°.

The following bases are also found in opium, at least occasionally: *codamine*, $C_{19}H_{23}NO_3$, *lanthopine*, $C_{23}H_{25}NO_4$, *laudanine*, $C_{20}H_{25}NO_3$, *meconidine*, $C_{21}H_{23}NO_4$, *opianine* and *porphyroxine*, but they are of small importance, and comparatively little is known respecting them.*

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* See Hesse, Ann. Ch. Pharm., cliii. 71; Gmelin's Handbook, xviii. 192, 197, 199, 202, 210; Watts's Dictionary of Chemistry, Supplement, p. 883.

3. *Cinchona Bases.*

The barks of the various species of cinchona contain a number of alkaloïds, associated with quinic acid and cinchona-tannin. The best known of these bases are:

Quinine,	$C_{20}H_{24}N_2O_2$.	Cinchonine,	$C_{20}H_{24}N_2O$.
Quinidine,	$C_{20}H_{24}N_2O_2$.	Cinchonidine,	$C_{20}H_{24}N_2O$.

Quinine is found chiefly in yellow cinchona-bark (from *China regia*); cinchonine in the grey bark (from *China Huanoco*).

The bases are extracted by digesting the pulverised bark with dilute hydrochloric acid, and precipitating the filtered solution with sodium carbonate, or magnesia. The precipitate, consisting of quinine, cinchonine, and a few other substances, is boiled with alcohol, and the solution is saturated with sulphuric acid, and evaporated. On cooling, it first deposits sulphate of quinine, and afterwards the cinchonine salt. The free bases are easily separated by ether, which dissolves only the quinine. Quinidine and cinchonidine are found in the last mother-liquors of the sulphuric acid solution.

Cinchonine crystallises in small, brilliant, transparent, four-sided prisms. It is very slightly soluble in water, dissolves readily in boiling alcohol, and has but little taste, although its salts are excessively bitter. It is a powerful base, neutralising acids completely, and forming a series of crystallisable salts. It turns the plane of polarisation strongly to the right.

Quinine much resembles cinchonine; but does not crystallise so well; it is much more soluble in water: tastes intensely bitter; turns the plane of polarisation strongly to the left.

Quinine sulphate is manufactured on a very large scale for medicinal use; it crystallises in small white needles, which give a neutral solution. It contains $2C_{20}H_{24}N_2O_2.SO_4H_2+7aq$. Its solubility is much increased by the addition of a little sulphuric acid, whereby the acid salt, $C_{20}H_{24}N_2O_2.SO_4H_2+7aq.$, is formed. Solutions of quinine sulphate exhibit a splendid blue fluorescence. On adding to the solution of a quinine salt, first chlorine-water and then ammonia, a fine green colour is produced. Iodine added to a solution of quinine sulphate, forms a crystalline substance of a brilliant emerald colour, which appears to have the composition $2C_{20}H_{24}N_2O_2.3H_2SO_4.I_6+3$ aq. This compound, called *Herapathite*, after its discoverer, possesses the optical properties of tourmaline.

Cinchonine and quinine yield with methyl iodide, the compounds $C_{20}H_{24}(CH_3)N_2OI$ and $C_{20}H_{24}(CH_3)N_2O_2I$, which are converted by silver oxide into soluble bases analogous to tetrethylammonium hydroxide: they are therefore tertiary amines.

Quinidine and *Cinchonidine*, isomeric respectively with quinine and cinchonine, are obtained from commercial quinoïdine, a resinous product contained in the mother-liquors of the quinine preparation.

Quinidine (or Conchinine) crystallises in large prisms moderately soluble in alcohol, sparingly in ether. Its salts are more soluble than those of quinine. The solutions are strongly dextrogyrate. With chlorine-water and ammonia quinidine reacts like quinine.

Cinchonidine, occurring also in the bark of *China Bogota*, is very much like cinchonine. Its solutions are strongly levogyrate. The acid sulphates of these four bases, heated first to 100°, to expel water of crystallisation, and then to about 135°, are converted into the sulphates of two amorphous bases, quinicine and cinchonicine, isomeric with quinine and cinchonine respectively, quinicine, $C_{20}H_{24}N_2O_2$, being formed from quinine and quinidine, cinchonicine, $C_{20}H_{24}N_2O$, from cinchonine and cinchonidine. The solutions of both these bases are feebly dextrogyrate.

All the four bases, when distilled with caustic potash, yield bases of the chinoline series (p. 611).

Strychnos Bases.

Strychnine, $C_{21}H_{22}N_2O_2$, and **Brucine,** $C_{22}H_{26}N_2O_4$, also called *Strychnia* and *Brucia*, are contained, together with several still imperfectly known bases, in *Nux vomica*, in *St Ignatius' bean*, and in *false Angustura bark.* To prepare them, nux vomica seeds are boiled in dilute sulphuric acid until they become soft: they are then crushed, and the expressed liquid is mixed with excess of calcium hydrate, which throws down the alkaloïds. The precipitate is boiled in spirits of wine of sp. gr. 0·850, and filtered hot. Strychnine and brucine are then deposited together in a coloured and impure state, and may be separated by cold alcohol, in which the latter dissolves readily.

Pure strychnine crystallises under favourable circumstances in small but exceedingly brilliant octohedral crystals, which are transparent and colourless. It has a very bitter, somewhat metallic taste (1 part in 1,000,000,000 parts of water is still perceptible), is slightly soluble in water, and fearfully poisonous. It dissolves in hot and somewhat dilute spirit, but not in absolute alcohol, ether, or solution of caustic alkali. This alkaloïd may be readily identified by moistening a crystal with concentrated sulphuric acid, and adding to the liquid a crystal of potassium dichromate, when a deep violet tint is produced, which disappears after some time.

Strychnine forms neutral crystalline salts, containing one equivalent of acid. The nitrate, $C_{21}H_{22}N_2O_2.NO_3H$, is sparingly soluble in water and in alcohol. Potassium thiocyanate added to the solutions throws down crystalline thiocyanate of strychnine.

Brucine, $C_{22}H_{26}N_2O_4$, crystallises in efflorescent prisms or tables containing $4H_2O$, easily soluble in alcohol, slightly in water, insoluble in ether; also very poisonous. Strong sulphuric acid colours the solutions red, and on adding stannous chloride to the red liquid, a violet precipitate is formed. Strong sulphuric acid dissolves brucine with reddish colour.

5. *Bases from various Plants.*

Veratrine or **Veratria**, $C_{32}H_{52}N_2O_8$, is obtained from the seeds of *Veratrum Sabadilla*, and from the root of *V. album*. In the pure state it is a white or yellowish-white powder, which has a sharp burning taste, is very poisonous, and in small quantities occasions violent sneezing. It is insoluble in water, but dissolves in hot alcohol, in ether, and in acids: the solution has an alkaline reaction.

Jervine, $C_{30}H_{46}N_2O_3$, occurring together with veratrine, in the root of *Veratrum album*, forms small prisms soluble in alcohol. Its salts are slightly soluble in water.

Piperine, $C_{17}H_{19}NO_3$, occurs in *Piper niger* and other kinds of pepper, from which it may be extracted by alcohol. It crystallises in four-sided prisms, melting at 100°, easily soluble in alcohol and ether, insoluble in water; dissolves with dark red colour in strong sulphuric acid. Heated with soda-lime it gives off piperidine, and by boiling with alcoholic potash, it is resolved into piperidine and piperic acid (p. 545):

$$C_{17}H_{19}NO_3 + H_2O = C_{12}H_{10}O_4 + C_5H_{11}N.$$

Piperidine, $C_5H_{11}N = C_5H_{10}NH$, is a liquid which boils at 106°, dissolves easily in alcohol and ether, has a strong alkaline reaction, and forms neutral crystalline salts with 1 eq. of acid. It is a secondary amine, one of its hydrogen-atoms being replaceable by acid and alcoholic radicles. *Methyl-piperidine*, $C_5H_{10}N.CH_3$, and *ethyl-piperidine*, $C_5H_{10}.N.C_2H_5$, are colourless liquids, the former boiling at 118°, the latter at 28°. Benzoyl-piperidine, $C_5H_{10}.N_2.C_7H_5O$, is crystalline. Piperine is a similar derivative containing the radicle of piperic acid, $C_5H_{10}.N_2.C_{12}H_9O_3$.

Atropine or **Daturine**, $C_{17}H_{23}NO_3$, occurring in the deadly nightshade (*Atropa Belladonna*) and in the thorn apple (*Datura Stramonium*), crystallises in thin prisms, melting at 90°. It is bitter, very poisonous, and in small quantity produces dilatation of the pupil. By heating with baryta-water or hydrochloric acid, it is resolved into tropic acid and tropine (p. 538):

$$C_{17}H_{23}NO_3 + H_2O = C_9H_{10}O_3 + C_8H_{15}NO.$$

Tropine is a strong mono-acid base, crystallising from ether in tables, melting at 61°.

Sinapine, $C_{16}H_{23}NO_5$, occurs in white mustard seed in the form of thiocyanate, which may be dissolved out by alcohol. The base, separated from the thiocyanate or other salt by alkalis, remains dissolved, and decomposes on evaporation. By boiling the salts with alkalis, the sinapine is resolved into choline (p. 222) and sinapic acid, $C_{11}H_{12}O_2$:

$$C_{10}H_{23}NO_5 + 2H_2O = C_5H_{15}NO_5 + C_{11}H_{12}O_2.$$

Sinapic acid is bibasic, and crystallises in thin prisms, soluble in hot water and in alcohol.

There are numerous other alkaloïds, more or less known, occurring in plants; the following short notice of a few of them must suffice:

Hyoscyamine.—A white, crystallisable substance, from *Hyoscyamus niger;* it occurs likewise in *Datura Stramonium.*

Solanine, $C_{43}H_{71}NO_{16}$(?).—A pearly, crystalline substance, from various solanaceous plants; resolved by boiling with dilute acids into glucose and solanidine: $C_{43}H_{71}NO_{16} + 3H_2O = 3C_6H_{12}O_6 + C_{25}H_{41}NO$.

Aconitine, $C_{30}H_{47}NO_7$.—A crystalline, very poisonous alkaloïd, from *Aconitum Napellus.*

Delphinine.—A yellowish, fusible substance, from the seeds of *Delphinium Staphisagria.*

Emetine.—A white and nearly tasteless powder, from ipecacuanha root.

Curarine.—The arrow-poison of Central America.

Pectous Substances.

The pulp of fleshy fruits in the unripe state, also of fleshy roots and other vegetable organs, contains a substance called pectose, which is insoluble in water, but under the influence of acids and other reagents, is transformed into a soluble substance pectin, identical with that which exists in ripe fruits and imparts to their juice the property of gelatinising when boiled.

Pectin may be obtained by boiling the pulp of carrots or turnips with a slightly acid liquid—or better, from the juice of ripe pears, by precipitating the lime with oxalic acid, then the albuminous substances with tannic acid, and adding alcohol, whereupon the pectin separates in long threads or as a jelly. When dry it forms an amorphous, tasteless mass, soluble in water, and precipitated therefrom by alcohol or by basic acetate of lead. On boiling the aqueous solution, the pectin is converted into parapectin, which, as well as pectin itself, is converted by boiling with dilute acids, into metapectin, which has an acid reaction, and is precipitated by barium chloride. These three substances are said to be isomeric, and represented by the empirical formula, $C_2H_3O_2$.

According to Frémy, all vegetable tissues which contain pectose contain also a ferment called pectase, similar in its mode of action to diastase and emulsin. It is an amorphous substance, which may be precipitated by alcohol from fresh carrot-juice. Under the influence of this ferment—or of dilute caustic alkalis at 30°—pectin is transformed into pectosic acid, $C_{32}H_{46}O_{28}.3H_2O$, and afterwards into pectic acid, $C_{16}H_{18}O_{13}.2H_2O$, which, by prolonged boiling with water, is converted into parapectic acid, $C_{24}H_{30}O_{21}.2H_2O$. The final product of the transformation of pectous substances is metapectic acid, $C_8H_{10}O_7.2H_2O$, which reduces alkaline copper solutions, and is resolved by alkalis into formic and protocatechuic acids. The composition of all these bodies is, however, very uncertain.

Bile Constituents.

1. BILIARY ACIDS.—Bile, the fluid secretion of the liver, contains—in addition to fats, mucous substances, proteids, urea, and choline—the sodium salts of two peculiar acids, called glycocholic and taurocholic; also certain colouring matters, and an aromatic alcohol called cholesterin, already described (p. 507.)

Glycocholic Acid, $C_{26}H_{43}NO_6$.—When fresh ox-bile perfectly dried is exhausted with cold absolute alcohol, and mixed after filtration with ether, it first deposits a brownish, tough, resinous mass, and after some time, stellate crystals, consisting of the glycocholates and taurocholates of sodium and potassium. On dissolving these salts in water and adding dilute sulphuric acid, glycocholic acid separates after twenty-four hours in the crystalline state, while taurocholic acid remains dissolved.

Glycocholic acid crystallises in white slender needles, sparingly soluble in water, easily in alcohol. It has a faint acid reaction and bitter-sweet taste. It is monobasic; its alkali-salts are very soluble in water, and have a very sweet taste. On adding to glycocholic acid a solution of sugar and then strong sulphuric acid, a purple-red coloration is produced (Pettenkofer's bile-reaction).

Glycocholic acid is resolved by boiling with alkalis into glycocine and cholic acid, $C_{24}H_{40}O_5$:

$$C_{26}H_{43}NO_6 + H_2O = C_2H_3(NH_2)O_2 + C_{24}H_{40}O_5.$$

Cholic acid crystallises in shining quadratic octohedrons containing $2\frac{1}{2}$ mol. water, soluble in alcohol and ether.

Glycocholic acid is also resolved into glycocine and cholic acid by boiling with acids, but the cholic acid is then converted, by abstraction of water, into dyslysin, $C_{24}H_{36}O_3$, an amorphous substance which is reconverted into cholic acid by boiling with alcoholic potash.

Taurocholic Acid, $C_{26}H_{45}NSO_7$, may be precipitated by basic lead acetate, after the glycocholic acid, mucus, and colouring matters have been removed by the neutral acetate. It forms slender needles, having a sweetish-bitter taste, and easily soluble in water and in alcohol. By boiling with water it is resolved into cholic acid and taurine (p. 173):

$$C_{26}H_{45}NSO_7 + H_2O = C_{24}H_{40}O_5 + C_2H_4(NH_2).SO_3H,$$

the cholic acid being, however, for the most part converted by dehydration into dyslysin. The same decomposition takes place in the putrefaction of bile.

Pig's bile contains two acids analogous to the above, viz., hyoglycocholic acid, $C_{27}H_{43}NO_5$, and hyotaurocholic acid, $C_{27}H_{45}NSO_6$, which are resolved by boiling with acids into hyocholic acid, $C_{25}H_{40}O_4$, and glycocine or taurine respectively.

Goose-bile contains a similar acid, $C_{29}H_{49}NSO_6$, called chenotaurocholic acid, which is resolved by alkalis into taurine and chenocholic acid, $C_{27}H_{44}O_4$.

Lithofellic acid, $C_{20}H_{36}O_4$, an acid nearly related to the biliary acids, occurs, together with ellagic acid, in Oriental bezoar-stones (p. 546). It may be extracted by hot alcohol, and crystallises in short prisms, melting at 204° ; gives, with sugar-solution and strong sulphuric acid, a purple-red colour, similar to that produced with glycocholic acid.

BILE PIGMENTS.—*Bilirubin*, $C_{16}H_{18}N_2O_3$, the principal colouring matter of the bile, forms dark red prisms, insoluble in water, sparingly soluble in acohol and ether, easily in chloroform and carbon sulphide. It dissolves in alkalis, forming a yellowish-red solution, which, when agitated in contact with the air, yields a green precipitate of *biliverdin*, $C_{16}H_{20}N_2O_5$. *Bilifuscin*, $C_{10}H_{20}N_2O_4$, is a dark green mass, insoluble in water and in chloroform, easily soluble in alcohol.

On heating an alkaline solution of these bile-pigments with nitric acid, a green colour is produced, changing to blue, violet, red, and ultimately to yellow. This reaction serves for the detection of bile.

Gelatinous Substances.

The bone-cartilages, tendons, connective tissue, and skin of the animal body dissolve, for the most part, when boiled for a long time with water, yielding a solution which solidifies, on cooling, to a transparent tremulous mas scalled gelatin or glutin; the non-hardening cartilages yield a similar substance, called chondrin.

These substances contain in 100 parts:

	C	H	N	O
Gelatin, . .	50·0	6·6	18·3	25·1
Chondrin, . .	49·1	7·1	14·4	29·4

Their molecular weights and structural formulæ are unknown.

Gelatin, Bone-gelatin or **Glutin,** precipitated from its aqueous solution by alcohol, forms a colourless, transparent mass, without taste or smell. It swells up in cold water, and dissolves on boiling to a viscid liquid, which solidifies to a jelly on cooling. By prolonged boiling with a small quantity of nitric acid, or, by the addition of concentrated acetic acid, the solution loses the property of gelatinising. The aqueous solution turns the plane of polarisation to the left. It is precipitated by alcohol, mercuric chloride, mercuric nitrate, and mercurous nitrate, but not by alum or by lead acetate, either neutral or basic. Tannic acid throws down, even from very dilute solutions of gelatin, a tough yellowish precipitate, consisting of a compound of the two bodies. The tissues which yield gelatin likewise unite with tannic acid, and withdraw it completely from its solutions, forming leather.

Gelatin boiled with sulphuric acid or with alkalis yields leucine and glycocine, together with other products of unknown constitution. By destructive distillation it yields several amines belonging to the fatty and pyridine series. By oxidation with MnO_2 and sulphuric acid, or with chromic acid, it yields the same products as the proteids (p. 625).

Isinglass is a very pure gelatin obtained from the dried swimming bladder of the sturgeon: it dissolves in water merely warm. *Size* is an impure gelatin, prepared from the clippings of hides and similar matters. *Glue* is the same substance dried by exposing it in thin slices on nettings to a current of air.

Chondrin, obtained from the cartilages of the ribs and joints, is very much like gelatin, but differs from it in being precipitated from its aqueous solution by acetic acid, alum, lead acetate, and other metallic salts, but not by mercuric chloride. Its products of decomposition are, for the most part, the same as those of gelatin; with sulphuric acid, however, it yields no glycocine, but only leucine. When boiled with hydrochloric acid it yields glucose.

Silk-gelatin or **Sericin**, $C_{15}H_{25}N_5O_8$, is extracted from silk by boiling with water, and precipitated by alcohol as an amorphous powder. It swells up in water, dissolves on boiling, and solidifies to a jelly; is precipitated by potassium ferrocyanide, basic lead acetate, and several other metallic salts. By boiling with sulphuric acid it yields leucine, tyrosine, and amidoglyceric acid or serine (p. 356).

Fibroin, $C_{15}H_{23}N_3O_6$, the chief constituent of silk (about 66 per cent.), is obtained by repeatedly digesting silk with water at 130°, and exhausting the residue with alcohol and ether: it then remains as a white shining mass. It dissolves in strong sulphuric acid and in alkalis, and is precipitated on saturating the solutions. When boiled with sulphuric acid it yields leucine, tyrosine, and glycocine.

Proteids or Albuminoids.

These substances form the chief part of the solid constituents of the blood, muscles, nerves, glands, and other organs of animals; they occur also in small quantities in almost every part of vegetables, and in larger quantities in the seeds. They are formed exclusively in plants, and undergo but little alteration when consumed as food and assimilated by animals.

The several bodies of this class resemble one another closely in their properties, and more especially in their percentage composition, which is comprised between the following limits:

Carbon,	52·7	to	54·5
Hydrogen,	6·9	„	7·3
Nitrogen,	15·4	„	16·5
Oxygen,	20·9	„	23·5
Sulphur,	0·8	„	1·6

These numbers may be approximately represented by the empirical formula $C_{72}H_{112}N_{18}O_{22}S$. The proteids also contain a small quantity of phosphorus, but apparently only mechanically mixed with them as calcium phosphate. Their molecular weights and constitution are not yet known; but recent investigations have thrown some light on the question, and indicate at least the direction in which its solution is to be sought. According to Hlasiwetz and Habermann, all proteids, when boiled with dilute sulphuric acid, or better, with hydrochloric acid, and a small quantity of stannous chloride, are resolved exactly into aspartic acid, glutamic acid (p. 360), leucine, tyrosine, and ammonia, and may therefore be regarded as formed by the combination of these substances, with elimination of water. Schützenberger, by heating proteids with baryta-water to 150° (whereby ⅕ of the nitrogen was evolved as ammonia), obtained essentially the same products of decomposition, and likewise intermediate products resulting from a less complete decomposition. The relative quantities of ammonia and carbon dioxide corresponded exactly with those which are evolved in the resolution of urea into $2NH_3$ and CO_2. This result tends to show that albumin is a complex ureide, containing one-fifth of its nitrogen in the form of urea.

Proteids are precipitated from solution: 1. By excess of mineral acids. 2. By potassium ferrocyanide with acetic acid or a little hydrochloric acid. 3. By acetic acid, with a considerable quantity of concentrated solutions of neutral salts of the alkalis and alkaline earths, gum arabic, or dextrin. 4. When boiled with mercuric nitrate (Millon's reagent *), they all give a deposit which turns red after a while, the supernatant liquors also becoming red. They rotate the plane of polarisation more or less to the left.

Proteids may be conveniently divided into the following classes:

CLASS I. ALBUMINS.—Soluble in water.

1. **Serum Albumin** is the most abundant albuminous substance in animal bodies. It can be obtained tolerably pure from blood-serum by precipitation with lead acetate, washing with water, suspending the precipitated lead-compound in water, and decomposing it with carbonic acid; then by filtration a very cloudy solution of albumin is obtained.

Serum albumin forms a yellow elastic transparent substance, which when perfectly dry can be heated to 100° without change. It is soluble in water, and precipitable by alcohol; long continued action of alcohol changes it into coagulated albumin. Its specific rotation is $-56°$ for yellow light. It is not precipitated by carbonic, acetic, tartaric, or phosphoric acid, or by other mineral acids, when very dilute, and added in small quantity; large quantities of acid precipitate it immediately; nitric acid acts most strongly.

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* Prepared by gently warming mercury with an equal quantity of strong nitric acid till it is dissolved, then diluting the liquid with twice its bulk of water, and leaving the precipitate to settle. The clear supernatant liquid is Millon's reagent.

† Hoppe-Seyler, Handbuch der physiologischen Chemie.

2. **Egg Albumin** differs from serum albumin by gradually giving a precipitate when agitated with ether; oil of turpentine also coagulates it. Serum albumin dissolves easily in strong nitric acid, whilst egg albumin is nearly insoluble therein. The specific rotation of egg albumin is $-35{\cdot}5°$ for yellow light.

The so-called *vitellin* contained in solution in the yolk of egg is a mixture of albumin and casein.

3. **Plant Albumin** occurs in nearly all vegetable juices, especially in potatoes and in wheat-flour. It coagulates by heat, and bears a close resemblance to egg albumin.

CLASS II. GLOBULINS.—Insoluble in water, soluble in very dilute acids and alkalis, soluble in dilute (1 per cent.) solutions of sodium chloride and other neutral salts.

1. **Myosin.**—This substance was first separated by Kühne from other albuminous matters occurring in the protoplasma or contractile muscular substance that causes the *rigor mortis.* To prepare it, well cut-up flesh is carefully washed with water, and the mass is then placed in a mixture of one volume of concentrated solution of common salt to two volumes of water; these are continually rubbed together and filtered through linen; the slimy filtrate is allowed to drop into a large quantity of distilled water. The myosin is redissolved in solution of sodium chloride, and reprecipitated by much water. It is insoluble in water, soluble in solution of common salt under 10°, soluble in very dilute hydrochloric acid, but in this solution it passes by degrees into acid albumin or syntonin; in dilute alkali, myosin, like other albuminous matters, is soluble, being changed into albuminate. By heat it is changed into coagulated albumin. It is also coagulated by alcohol.

2. **Globulin** (*Paraglobulin, Paraglobin*).—When fresh blood-serum is diluted tenfold with water, and a brisk stream of carbonic acid passed through it, a fine granular precipitate is formed, which may be separated by decantation and filtration, and washed with water. The same substance may be prepared by saturating blood-serum with sodium chloride (or magnesium sulphate, &c.), as in the case of myosin. A certain amount of the salt always clings to the precipitate.

Globulin is exceedingly soluble in dilute saline solutions (from which it may be precipitated unchanged by carbonic acid gas or *exceedingly* dilute acids). It is insoluble in water, but dissolves when the water is saturated with oxygen, and may be precipitated by carbonic acid.

In excessively dilute alkalis globulin dissolves without alteration; in solutions containing about 1 per cent. of the alkali, it dissolves as albuminate. By dilute acids, however feeble it is changed in solution into acid-albumin. Suspended in water and heated to 70°, it enters into the insoluble or coagulated state.

Globulin is present, not only in serum of blood, but also in aqueous humour, in the juice of the cornea, connective tissue, &c. Derived from the first of these sources, globulin is fibrinoplastic *i.e.*, it has the power of acting in concert with certain fluids (fibrinogenous) in such a manner as to give rise to fibrin (p. 628). The crystalline lens contains a substance which is not fibrinoplastic, but in many other respects closely resembles the globulin just described.

3. **Fibrinogen.**—When hydrocele fluid, pericardial fluid, or any other fluid capable of giving a clot with blood-serum or paraglobulin, is treated by the method adopted for globulin, a similar substance is produced which resembles globulin in every respect, except that the carbonic acid precipitate is more difficult to obtain and more flaky, and that the substance is more readily thrown down from the liquids in which it is formed, by a mixture of alcohol and ether; also by the fact that it is fibrinogenous, *i.e.*, produces fibrin when mixed with fibrinoplastic globulin.

CLASS III. DERIVED ALBUMINS.—Insoluble in water, and in solutions of sodium chloride; soluble in dilute acids and alkalis.

1. **Acid-albumin.**—If a small quantity of dilute acid (hydrochloric or acetic) be added to serum- or egg-albumin, no precipitation or coagulation takes place, and on gradually raising the temperature of the mixture to 70°, it will be found that coagulation at that or at a higher temperature has been entirely prevented. At the same time the influence of the fluid on polarised light has been altered. The rotation to the left has become increased to 72°.

On carefully neutralising the cooled mixture, the whole of the proteid matter is thrown down as a white, flocculent, frequently gelatinous precipitate. The action of the acid has converted the albumin soluble in water into a substance insoluble in water. The precipitate is very readily soluble in excess of the alkali used for neutralisation, may be reprecipitated by again neutralising with an acid, again redissolved by excess, and so on. It is also soluble in dilute solutions of alkaline carbonates. It is insoluble in sodium chloride solution, and may be precipitated from its solutions by the addition of that salt. Suspended in water and heated to 70°, it enters into the coagulated or insoluble condition.

All the globulins of Class II. are readily soluble in dilute acids; but by the act of solution they are at once converted into acid-albumin, the precipitate formed by neutralisation being no longer soluble in neutral saline solutions.

2. **Alkali-Albumin** or **Albuminate. Casein.**—When albuminous substances, egg- or serum-albumin, for example, are treated with dilute caustic alkali instead of acid, coagulation by heat is similarly prevented, and the whole of the proteid may in like manner be thrown down on neutralisation. Some of the bodies thus produced agree well together, and cannot be distin-

guished from the casein of milk, although most probably casein is not identical with artificial albuminate, and the bodies which are produced by the action of potash on different albuminous substances may differ slightly one from the other, as is evident in the difference of their rotatory action on polarised light.

Casein occurs most plentifully in the milk of animal feeders, and is best obtained from milk by precipitating with crystalline magnesium sulphate, filtering and washing with a concentrated solution of salt, then dissolving the precipitate in water; the butter is filtered off, and the clear solution precipitated by dilute acetic acid.

Dried casein and albuminate are yellow, transparent, and hygroscopic, swelling up in water, but not dissolving. When precipitated in a flocky state, they dissolve easily in water if it contains a little alkali. The precipitate which forms on neutralising the alkaline solution, dissolves easily in an excess of acetic acid or dilute hydrochloric acid. On the addition of an excess of mineral acid, or on neutralisation with an alkali, these solutions give a precipitate.

The neutral or feebly alkaline albuminate, and casein in alkaline solution, are precipitated in the cold by alcohol: when hot they are dissolved. By fusion with potassium hydrate, casein yields valeric and butyric acids, besides other products.

The most striking property of casein is its coagulability by certain animal membranes, as is seen in the process of cheese-making, in preparing the *curd*, the coagulation being effected by an infusion of the stomach of the calf called *rennet*.

Plant-casein or Legumin is found chiefly in the seeds of leguminous fruits, from the juice of which it may be precipitated by acetic acid or by rennet.

Class IV.—**Fibrin.**—Insoluble in water; sparingly soluble in dilute acids and alkalis, and in neutral saline solutions.

This is the substance to which the clotting of blood is due. It may be obtained by washing blood-clots, or more readily by stirring with a bundle of twigs, blood just shed, before it has had time to clot. The fibrin, which adheres in layers to the twigs, may then be stripped off and washed till perfectly white. The formation of fibrin is due to the contact of fibrinoplastic and fibrogenous substance. When these two substances come into contact in any fluid, they combine, quickly or slowly, according to the greater or lesser quantity of each substance in the fluid, to form fibrin.

Fibrin differs from all other solid proteids in having a filamentous structure, and in possessing remarkable elasticity. It is insoluble in water, dilute hydrochloric acid, and aqueous sodium chloride, but dissolves at 40° in aqueous potassium nitrate.

Plant-fibrin occurs as an insoluble substance in plants, especially in the seeds of cereal grasses. When wheat-flour is stirred up to a paste with water, and kneaded for some time, the starch granules and soluble albumin are removed, and there remains a tenacious mass called gluten; and by boiling this substance with dilute alcohol to remove vegetable gelatin (gluten) and extracting the fats with ether, the plant fibrin is obtained in the form of a greyish-white, tough, elastic mass. It dissolves in very dilute hydrochloric acid, and in dilute alkalis, and is precipitated from these solutions by neutral salts, and by acetic acid. By boiling with dilute sulphuric acid, plant fibrin is resolved into leucine, tyrosine, and glutamic acid.

Class V. **Coagulated Proteid.**—Coagulated albumin is formed from albumin, syntonin, fibrin, myosin, &c., by heating their neutral solutions to boiling, or by the action of alcohol. Egg albumin is also changed into coagulated albumin by strong hydrochloric acid and by ether. The albuminates, and also casein, when precipitated by neutralisation, pass into coagulated albumin when heated. The coagulated albuminous substances are insoluble in water, alcohol, and other indifferent fluids, scarcely soluble in dilute potash, soluble with great difficulty in ammonia. In acetic acid they swell up, and gradually dissolve. They are mostly insoluble in dilute hydrochloric acid; but when pepsin is also present at blood heat, they change first into syntonin, and then into peptone. They are dissolved by strong hydrochloric acid, and by caustic potash they are changed into albuminates.

Class VI. **Peptones.**—By the action of the acid gastric juice, all albuminous substances are changed into bodies called peptones. These are found only in the stomach and in the contents of the small intestines. They can no longer be detected in the chyle. They are highly diffusible, easily soluble in water, insoluble in alcohol or ether; but alcohol separates them with difficulty from the watery solution; when precipitated they remain unchanged even after boiling. They are not precipitated either by acids or by alkalis. Acetic acid and potassium ferrocyanide give no precipitate; but corrosive sublimate and lead acetate with ammonia give precipitates.

The reactions of the several proteids above described may be tabulated as follows:—

Soluble in water:
  Aqueous solutions not coagulated by boiling, Peptones.
  Aqueous solutions coagulated by boiling, . Albumins.
Insoluble in water:
  Soluble in a 1 p. c. solution of sodium chloride, Globulines.
Insoluble:
  Soluble in hydrochloric acid (0·1 p. c.) in the cold:
    Soluble in hot spirit, ... Alkali-albumin.
    Insoluble in hot spirit, ... Acid-albumin.

Insoluble in hydrochloric acid (0·1 p. c.) in the cold:	
Soluble in hydrochloric acid (0·1 p. c.) at 60°,	FIBRIN.
Insoluble in hydrochloric acid (0.1 p. c.) at 60°; insoluble in strong acids; soluble in gastric juice, ...	COAGULATED ALBUMIN.

Substances relating to the Proteids.

Hæmoglobin, 54·2 oxygen, 7·2 hydrogen, 0·42 iron, 16·0 nitrogen, 21·5 oxygen, and 0·7 sulphur; also called *Hæmatoglobulin* and *Hæmatocrystallin.*—This substance forms the chief part of the red globules of the blood of vertebrata; usually it is obtained in an amorphous condition, but from the blood of some animals—as, for example, dogs, cats, rats, mice, and many fish—it can be separated in the crystalline form. Red crystals can be obtained from dog's blood by mixing the defibrinated blood with an equal quantity of water, adding 1 volume of alcohol to 4 volumes of the diluted blood, and leaving it at rest at 0° or lower. After 24 hours the hæmoglobin separates in small violet-red rhombic octohedrons. After drying over sulphuric acid it forms a brick-red powder. It dissolves in cold water, forming a red solution, from which it is precipitated in the crystalline form by alcohol. At ordinary temperatures the solution decomposes and turns brown.

The aqueous solution of hæmoglobin (or of blood) exhibits in its spectrum two absorption-bands situated between the Frauenhofer lines D and E (in the yellow and green).

Hæmoglobin unites with certain gases forming peculiar unstable compounds. The solution containing oxygen has a deep red colour; the solution free from oxygen is dark purple (arterial and venous blood); the absorption-bands are exhibited only by the oxygenated solution. Carbon monoxide displaces the oxygen, and forms with the hæmoglobin a compound which, on addition of alcohol separates in bluish crystals: this appears to be the cause of the deleterious action of carbon monoxide on animals.

Oxygenated hæmoglobin is resolved by dilute acids or alkalis into two proteids, fatty acids, and a colouring matter called hematin, which in the dry state is a dark blue powder. It contains 9 per cent. of iron, and appears to have the composition $C_{34}H_{34}FeN_4O_5$.

When hæmoglobin (or blood) is warmed with strong acetic acid and solution of common salt, a substance called hemin separates in yellowish-red microscopic rhombic crystals, the formation of which serves as a delicate indication of the presence of blood.

Related to the proteids are also many ferments, such as emulsin or synaptase, occurring in almonds; diastase (p. 206), which is formed from vegetable fibrin in the germination of seeds, and is characterised by the property of converting starch and dextrin into sugar; myrosin from mustard-seeds (p. 104); ptyalin, the ferment of saliva, which also converts starch into dextrin and sugar; pepsin, which is contained in gastric juice, and possesses the power, in conjunction with hydrochloric acid, of dissolving the insoluble proteids and converting them into peptones.

Mucin is the chief constituent of animal mucus, and is precipitated by alcohol and dilute acetic acid.

The horny substances of horns, nails, hoofs, hairs, feathers, and the epidermis, are also nearly related to the proteids, having indeed the same composition, except that they contain more sulphur (2—5 p. c.). They dissolve easily in alkalis, with formation of sulphides. Nitric acid turns them yellow. Boiled with dilute sulphuric acid they yield leucine and tyrosine.

Brain Constituents.

When brain or spinal marrow is boiled with water, creatine, inosite, lactic acid, uric acid, and other substances, it dissolves, and from the residue ether extracts fats, cholesterin (p. 507), cerebrin, and lecithin. On cooling the solution, the two latter substances are first deposited, and may be separated by cold ether, which dissolves only the lecithin. The so-called *protagon* is a mixture of cerebrin and lecithin.

Cerebrin or **Cerebric Acid**, $C_{17}H_{33}NO_3$, is a light amorphous powder, without taste or smell; swells up like starch when boiled with water, and is converted by boiling with dilute acids into a saccharine substance, and other products.

Lecithin, $C_{42}H_{84}NPO_9$, is widely diffused in the animal organism, occurring especially in the brain nerves, yolk of eggs, blood-corpuscles, &c. It is best prepared by exhausting egg-yolk with a mixture of alcohol and ether, evaporating the ether, adding an alcoholic solution of platinic chloride, decomposing the yellow platinochloride $(C_{42}H_{83}NPO_8Cl)_2.PtCl_4$, with hydrogen sulphide, and evaporating the filtrate.

Lecothin is a waxy, indistinctly crystalline mass, which dissolves in alcohol and ether, and swells up in water, forming an opalescent solution or emulsion, from which it is precipitated by various salts of the alkali-metals. It unites both with bases and with acids.

By boiling with acids, or with baryta-water, lecithin is resolved into choline, glycerophosphoric acid, palmitic acid and oleic acid.

APPENDIX.

TABLE

OF THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES (FOWNES).

Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.	Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.	Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9453	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
0·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
0·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8793	67		

TABLE

OF THE PROPORTION BY VOLUME OF ABSOLUTE OR REAL ALCOHOL IN 100 VOLUMES OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES (GAY-LUSSAC) AT 59° F. (15° C.).

100 vol. Spirits.		100 vol. Spirits.		100 vol. Spirits.	
Spec. Grav.	Contain vol. of real Alcohol.	Spec. Grav.	Contain vol. of real Alcohol.	Spec. Grav.	Contain vol. of real Alcohol.
1·0000	0	0·9608	34	0·8956	68
0·9985	1	0·9594	35	0·8932	69
0·9970	2	0·9581	36	0·8907	70
0·9956	3	0·9567	37	0·8882	71
0·9942	4	0·9553	38	0·8857	72
0·9929	5	0·9538	39	0·8831	73
0·9916	6	0·9523	40	0·8805	74
0·9903	7	0·9507	41	0·8779	75
0·9891	8	0·9491	42	0·8753	76
0·9878	9	0·9474	43	0·8726	77
0·9867	10	0·9457	44	0·8699	78
0·9855	11	0·9440	45	0·8672	79
0·9844	12	0·9422	46	0·8645	80
0·9833	13	0·9404	47	0·8617	81
0·9822	14	0·9386	48	0·8589	82
0·9812	15	0·9367	49	0·8560	83
0·9802	16	0·9348	50	0·8531	84
0·9792	17	0·9329	51	0·8502	85
0·9782	18	0·9309	52	0·8472	86
0·9773	19	0·9289	53	0·8442	87
0·9763	20	0·9269	54	0·8411	88
0·9753	21	0·9248	55	0·8379	89
0·9742	22	0·9227	56	0·8346	90
0·9732	23	0·9206	57	0·8312	91
0·9721	24	0·9185	58	0·8278	92
0·9711	25	0·9163	59	0·8242	93
0·9700	26	0·9141	60	0·8206	94
0·9690	27	0·9119	61	0·8168	95
0·9679	28	0·9096	62	0·8128	96
0·9668	29	0·9073	63	0·8086	97
0·9657	30	0·9050	64	0·8042	98
0·9645	31	0·9027	65	0·8006	99
0·9633	32	0·9004	66	0·7947	100
0·9621	33	0·8980	67		

ADDITIONS AND CORRECTIONS.

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The pungent liquid called "Vinyl Alcohol," which Berthelot obtained by agitating acetylene with sulphuric acid and distilling the product with water, appears, from recent experiments by Lagermark and Elketoff (*Ber. d. deutsch. chem. Gesellschaft*, x. 637), not to be an alcohol at all, but to consist of crotonic aldehyde, formed by condensation of acetaldehyde, the first product of the reaction, and convertible, by oxidation with silver oxide, into solid crotonic acid.

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Propargyl Alcohol, $C_3H_4O = CH \equiv C.CH_2.OH$, the only known alcohol of the series $C_nH_{2n-2}O$, is formed by the action of KOH on brominated allyl alcohol, $CH_2{=}CBr.CH_2.OH$. It is a colourless, very fragrant liquid, soluble in water. Sp. gr. 0·963 at 21°. Boiling point 114°–115°. With silver nitrate it forms a white precipitate, $C_3H_2Ag.OH$, and with an ammoniacal solution of cuprous chloride, a yellow precipitate, $C_3H_4Cu.OH$, which explodes when heated. With PBr_3 it forms propargyl bromide, C_3H_3Br, a liquid boiling at 88°–90°; and with acetyl chloride, the acetic ether, $C_3H_3.O.C_2H_3O$, which boils at 125°.

Ethyl Propargylate, $C_3H_3.O.C_2H_5$, formed by the action of alcoholic potash on dichloroglycide, allyl tribromide, and several similar haloïd compounds, is a pungent liquid, boiling at 81°–85°, and having a sp. gr. of 0·83 at 7°. With silver nitrate it forms a white precipitate, $C_3H_2Ag.O.C_2H_5$, and with ammoniacal cuprous chloride a yellow precipitate, $C_3H_2Cu.O.C_2H_5$.

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Purpuroxanthic Acid, $C_{15}H_8O_6 = C_{14}H_7O_4.CO_2H$, is a constituent of commercial purpurin, from which it may be extracted by means of boiling alum-liquor. It is more soluble in boiling water than most madder colours; crystallises from hot alcohol in yellow needles; melts at 231°, and splits up at 232°–233° into CO_2 and purpuroxanthin. It dissolves in a boiling solution of ferric chloride with deep reddish-brown colour, and is reprecipitated by hydrochloric acid in yellow flocks.

Purpuroxanthic acid is most probably identical with *Munjistin*, a colouring matter extracted some years ago by Dr. Stenhouse from *Munjeet* or East Indian madder, this substance being also resolved by heat into CO_2 and purpuroxanthin (Schunck and Roemer, *Chem. Soc. Journal*, 1877, i. 666.

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Pseudopurpurin.—This is a constituent of crude purpurin, hitherto regarded as a dioxyalizarin or tetraoxyanthraquinone, $C_{14}H_8O_6$, but lately shown by Rosenstiehl (*Comptes rendus*, lxxxiv. 561) to consist of purpurin-carbonic acid, $C_{15}H_8O_7 = C_{14}H_7O_5.CO_2H$, inasmuch as it is resolved by heat into CO_2 and purpurin. It is also readily converted into purpurin by alkalis, even at ordinary temperatures.

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ERRATA.

Page 429, line 5, *for* give *read* gives.
Page 429, line 6, *for* gives *read* give.
Page 449, line 7, column 2, *for* $C_6H_4Cl_2(NO_2)$ *read* $C_6H_3Cl_2(NO_2)$.

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